Supporting Information for:

Interfacial Charge Separation and Recombination in InP and Quasi-type II InP/CdS Core/Shell Quantum Dot-Molecular Acceptor Complexes

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S1. Synthesis of InP and InP/CdS QDs

InP QDs were synthesized by the method developed by Peng et al, with slight modifications.[1] Briefly, a mixture of 58.4 mg (0.2 mmol) of Indium acetate ($InAc_3$), 0.137 g(0.6 mmol) of myristic acid (MA) and 7 mL of 1-octadecene (ODE) was heated at 140 °C under argon until it turned clear. The sample was pumped to vacuum for 1 hour and then switched back to argon purge. The temperature was raised to 285 °C at which point 0.1 mmol of tris(trimethylsilyl)phosphine (P(TMS)3)

dissolved in 0.5 mL ODE was swiftly injected. After the injection, the temperature was dropped down to 270 °C for the growth of the InP QDs. The reaction was stopped after 4 min by removing the heating mantle. InP QDs were precipitated out of the solution by adding ethanol. The precipitation was repeated for several times to remove excess ligands.

The as-synthesized InP QDs were used as core for CdS shell growth. CdS shell coating well achieved by successive ion layer adsorption and reaction (SILAR).[2] A cadmium precursor solution (0.04 M) was prepared by dissolving 0.077 g of CdO in 1.2 mL of OA and 15 mL of ODE at 300 °C to obtain a colorless solution. The precursor solution was then maintained at above 100 °C. A sulfur injection solution (0.015 M) was prepared by dissolving 18.6 mg of sulfur in 20 mL of ODE in an ultrasonic bath. The CdS shells were grown one layer at a time, by the successive injection of calculated amounts of cadmium and sulfur precursor solutions using air-free syringe pump (with a rate of 1mL/1h). The amount of precursors required was determined by estimated core size and shell volume. The shell growth was performed initially at 180 °C to maintain the core size and gradually increased up to 240 °C for the 4^{th} monolayer (ML). The time interval between two successive injections was 10 minutes. The InP/CdS QDs were also precipitated out of the solution by adding ethanol.

TEM images and diameter distribution histograms of InP and InP/CdS QDs are shown in Figure S1. Since InP QDs have zinc blende cubic lattice structure, they have relatively round shape. The CdS shell, however, has a wurzite hexagonal lattice structure, resulting in a prolate shape of the core/shell QDs. The InP core QDs have an average diameter of 2.6(±0.3) nm. After coating of nominal 4 MLs of CdS, the average diameter of core/shell QDs reach 5.8(±0.8) nm, corresponding to a shell thickness of 1.6 nm. Using the lattice constant of wurtize CdS (c=0.67 nm),[3] the average number of CdS monolayers was estimated to be 2.4 MLs.

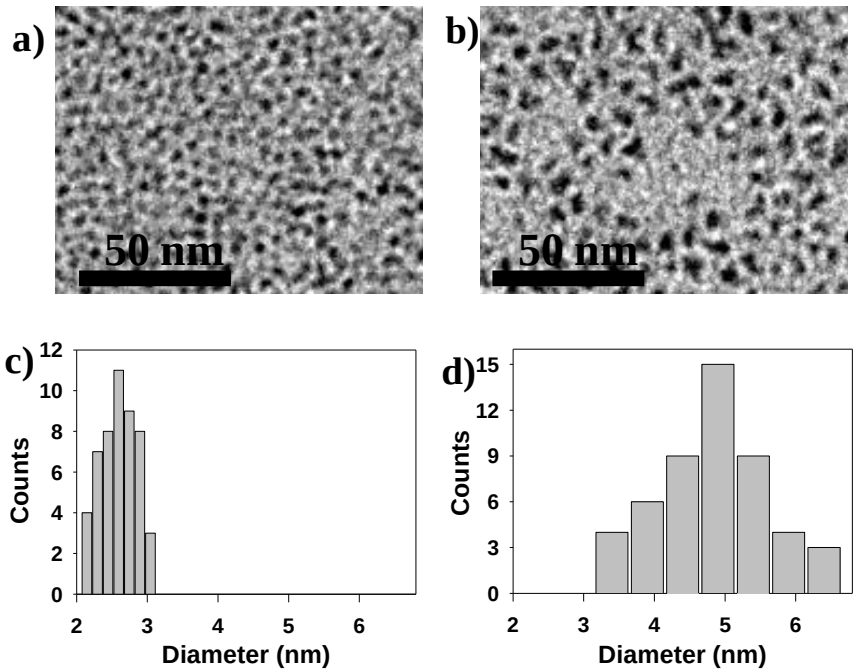

Figure S1. TEM images of InP core QDs (a) and InP/CdS core/shell QDs (b). Histograms of diameter distribution for InP core QDs (c) and InP/CdS core/shell QDs (d).

S2. Fitting kinetics of XB and PA signals of 400 excited InP QDs

The kinetics of PA signal shown in Figure 2 is fitted to eq (S1), which contains a nearly-instantaneous formation followed by a fast single-exponential decay and a highly-dispersive stretched-exponential decay.

$$\Delta A(PA) = A(PA) \bullet \{a_1 \exp(-t/\tau_1) + a_2 \exp[-(t/\tau_2)^{\alpha}] - \exp(-t/\tau_f)\} \qquad \text{(S1)}$$

The kinetics of XB (Figure 2) is fitted according to Eq (S2), containing bi-exponential formation and a stretched-exponential decay. The parameters of stretched exponential decay are constrained to be the same in both PA and XB kinetics.

$$\Delta A(XB) = A(XB) \bullet \{\exp[-(t/\tau_2)^{\alpha}] - b_1 \exp(-t/\tau_{f1}) - b_2 \exp(-t/\tau_{f2})\} \qquad \text{(S2)}$$

The fitted curves are shown in Figure 2b and the fitting parameters are tabulated in table S1.

Table S1. Fitting parameters for TA kinetics in InP QDs

	τ_{f1}/ps (b_1)	τ_{f2}/ps (b_2)	τ_1 /ps (a_1)	τ_2 /ns (a_2)	α
XB	0.33±0.08 (98.0±1.2%)	2.47±0.33 (2.0±0.15%)	NA	5.17±0.09 (100%)	0.387±0.002

PA	0.005±0.006 (100%)	NA	2.55±0.46 (16.2±2.5%)	5.17±0.09 (83.8±2.5%)	0.387±0.002

S3. TA spectrum and kinetics in InP QD- benzoquinone (BQ)

To assign PA signal, benzoquinone (BQ) is used to selectively remove the electrons from the excited QDs. Figure S2 shows the TA spectra and kinetics for InP QD-BQ complexes. Compared to free QDs, both XB and PA features decay faster decay faster due to electron transfer and their decay kinetics are the same except for the first 5 ps.

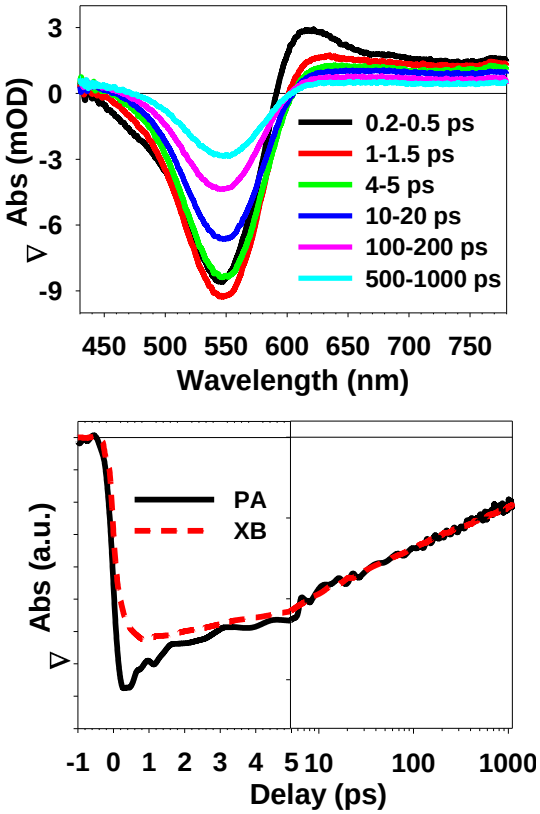

Figure S2. a) TA spectrum of InP-BZ complexes from 0.2 ps to 1000 ps after 400 nm excitation. Compared to free InP QDs, both XB and PA signals show faster decay due to electron transfer from excited InP to BZ. b) Kinetics of XB (red dashed line) and PA (black solid line) from 0 to 1000 ps.

S4. Fitting charge separation kinetics in 400 nm excited InP QD-MV^{2+} complexes

To extract charge separation rates in QD-MV^{2+} complexes, we simultaneously fit the kinetics at 730-760 nm (which is a sum of PA and $MV^{+\bullet}$ signals) and 545-560 nm (which is a sum of XB, PA, and $MV^{+\bullet}$ signals) using the model shown in scheme 1 of the main text. We assume that electron

arrives at 1Pe level instantaneously, through direct excitation or ultrafast relaxation from the higher lying states. 1Pe electrons have two decay channels, relaxation into 1Se level or interfacial electron transfer to MV^{2+} lowest unoccupied molecular orbital (LUMO). The relaxed 1Se electron can also transfer into MV^{2+} LUMO. Using this model, the signal at 730-760 nm can be fitted as:

$$\Delta A(730-760) = A(PA) * \left[0.16 \cdot \exp\left(-{}^{t}/_{\tau_0}\right) + 0.84 \cdot \sum_{i=1}^{3} a_i \exp\left(-{}^{t}/_{\tau_i}\right) - \exp\left(-{}^{t}/_{\tau_{fPA}}\right)\right] + A(PA) * \left[1 - \sum_{i=1}^{3} a_i \exp\left(-{}^{t}/_{\tau_i}\right)\right] \quad \text{(S3)}$$

Here the signal size A(PA), formation time τ_{fPA}, the amplitudes (0.16 and 0.84) and initial decay time constant (τ_0, attributed to hole trapping) are taken from the fitting parameters of PA signal in free InP QDs. The decay of the PA signal (a_i and τ_i) reflects the electron transfer kinetics. $A(MV^{+\bullet})$ is the $MV^{+\bullet}$ signal size which is taken to be the signal at 730-760 nm at 100 ps, when charge separation is completed and the extent of charge recombination is negligible.

The signal at 545-560 nm can be fitted as:

$$\begin{aligned}\Delta A(545-560) &= A(XB) \bullet [\sum_{i\neq 1} \frac{a_i}{1-a_1} \exp(-t/\tau_i) - \exp(-t/\tau_{fXB})] \\ &+ A(PA) \bullet [0.16 \bullet \exp(-t/\tau_0) + 0.84 \bullet \sum_{i=1}^{3} a_i \exp(-t/\tau_i) - \exp(-t/\tau_{fPA})] \\ &+ A(MV^{+\bullet}) \bullet [1 - \sum_{i=1}^{3} a_i \exp(-t/\tau_i)]\end{aligned} \quad \text{(S4)}$$

Here we have excluded the hot electron transfer process (i=1) from the XB bleach recovery kinetics. Because the amplitude of A(XB) is determined by the competition of hot electron relaxation and transfer, a constraint is added to the fitting:

$$A(XB) = A(XB)_{free} \bullet \frac{k_{f\,XB}}{k_{f\,XB} + k_{het}} \quad \text{(S5)}$$

Here $A(XB)_{free}$ is initial XB bleach amplitude in free InP QDs, $k_{f\,XB}$ the hot electron relaxation rate (0.38 ps) and k_{het} the hot electron transfer rate ($k_{het} = 1/\tau_1$).

Fitting the kinetics at 730-760 nm and 545-560 nm simultaneously by equations (S3-S5) yields satisfactory fit to the data shown in Figure 3b. a_i and τ_i are the only fitting parameters and their values are listed in Table S2. The averaged electron transfer time from $1S_e$ level is calculated as:

$$\tau_{ave(1S_e)} = \frac{a_2\tau_2 + a_3\tau_3}{a_2 + a_3} \quad \text{(S6)}$$

Table S2. Fitting parameters for TA kinetics in InP-MV^{2+} complexes

τ_1/ps (a_1)	τ_2/ps (a_2)	τ_3 /ps (a_3)	$\tau_{ave(1Se)}$/ps
0.40±0.13 (45±12 %)	0.92±0.21 (34.2±0.74 %)	28.7±3.8 (20.6±1.26%)	11.4±2.7

S5. Fitting kinetics of B1 and B2 signals of 400 nm and 525 nm excited InP/CdS QDs

B1 and B2 kinetics measured with 400 nm excitation can be fitted with exponential formation functions with different rise times followed by the same stretched exponential decay function:

$$\Delta A(B_{1(2)}) = A(B_{1(2)}) \bullet [\exp[-(t/\tau)^{\alpha} - \exp(-t/\tau_f)] \quad \text{(S7)}$$

The fitting parameters are tabulated in table S3.

Table S3. Fitting parameters for TA kinetics in InP/CdS QDs measured with 400 nm excitation

	τ_f/ps	τ /ns	α
B_1	0.173±0.012	10.1±0.1	0.283±0.001
B_2	0.452±0.025	10.1±0.1	0.283±0.001

Under 525 nm excitation, the kinetics at B1 and B2 transitions are identical and can be fitted with single exponential formation and multi-exponential decay:

$$\Delta A(B_{1(2)}) = A(B_{1(2)}) \bullet [\sum_i a_i \exp(-t/\tau_i) - \exp(-t/\tau_f)] \quad \text{(S8)}$$

The results are listed in Table S4.

Table S4. Fitting parameters for TA kinetics in InP/CdS QDs measured with 525 nm excitation

	τ_f /ps	τ_1 /ps (a_1)	τ_2 /ps (a_2)	τ_3 /ps (a_3)	τ_4 /ps (a_4)
B1(2)	0.040±0.032	1.26±0.14 (13.2±1.7%)	23.6±2.2 (16.4±1.3%)	405±34.2 (19.4±1.5%)	>>1000 (51.0%)

S6. Fitting charge separation kinetics in InP/CdS QD-MV^{2+} complexes

We fit the kinetics at 445-455 nm of the InP/CdS-MV^{2+} complexes as a sum of state-filling induced bleach of B1 transition, charge-separation induced Stark effect and $MV^{+\bullet}$ signal. Since the last two signals result from the charge separated state, they can be combined as A(CS). We account for both the electron transfer from the 1S electron level and hot electron transfer from higher levels, as shown in scheme 1. Within this model, the kinetics at 445-455 nm is given by:

$$\begin{aligned}\Delta A(B1) = A(B1) \bullet [\sum_{i\neq 1} \frac{a_i}{1-a_1} \exp(-t/\tau_i) - \exp(-t/\tau_{fB1})] \\ + A(CS) \bullet [1 - \sum_{i=1}^{4} a_i \exp(-t/\tau_i)]\end{aligned}, \quad \text{(S9)}$$

In Eq. (S8) A(CS) is taken to be the signal at 200 ps when charge separation is completed and the extent of charge recombination is negligible. We also added the constraint:

$$A(B1) = A(B1)_{free} \bullet \frac{k_{fB1}}{k_{fB1} + k_{het}} \quad \text{and} \quad k_{het} = 1/\tau_1 . \quad \text{(S10)}$$

where $A(B1)_{free}$ is the initial amplitude of B1bleach and k_{fB1} the hot electron relaxation rate, which have been independently determined by the kinetics of free InP/CdS QDs at the same probe wavelength. The kinetics in Figure 6b can be fitted by this model with a_i, τ_i as the only fitting parameter. The fitting parameters are listed in Table S5. The averaged electron transfer time from $1S_e$ level is calculated as:

$$\tau_{ave(1S_e)} = \frac{a_2\tau_2 + a_3\tau_3 + a_4\tau_4}{a_2 + a_3 + a_4} \quad \text{(S11)}$$

Table S5. Fitting parameters for charge separation kinetics in InP/CdS-MV^{2+} complexes.

τ_1/ps (a_1)	τ_2/ps (a_2)	τ_3 /ps (a_3)	τ_4 /ps (a_4)	$\tau_{ave(1Se)}$/ps
0.346±0.087 (33.3±7.5%)	1.33±0.21 (7.34±1.6%)	6.18±0.45 (20.7±3.1%)	23.2±3.8 (36.9±5.7%)	15.3±7.1

S7. Fitting charge recombination kinetics in QD-MV complexes

The decay kinetics of the radical signals (10 ps to 3000 ns for InP and 200 ps to 3000 ns for

InP/CdS) are fitted by multi-exponential decay functions. The fitting parameters are tabulated in table S6. The amplitude-weighted average lifetime (τ_{ave})is calculated as:

$$\tau = \frac{\sum_{i=1}^{3} a_i \tau_i}{\sum_{i=1}^{3} a_i} \quad \text{(S12)}$$

The average charge-separated state lifetime is 47.05 (±5.04) and 233.2 (±24.6) ns for InP and InP/CdS core/shell QDs , respectively.

Table S6. Fitting parameters for charge recombination kinetics in QD-MV^{2+} complexes.

	τ_1 /ns (a_1)	τ_2 /ns (a_2)	τ_3 /ns (a_3)	τ_{ave}/ns	$\tau_{1/2}$/ns
InP	3.21±0.19 (50.9±0.016%)	24.3±2.0 (37.5±0.015%)	313±36 (11.6±0.007%)	47.1 ±5.1	5.89±0.57
InP/CdS	8.72±0.42 (36.2±0.027%)	63.5±4.1 (39.7±0.013%)	850±94 (24.1±0.023%)	233±25	33.4±2.3

References:

(1) Battaglia, D.; Peng, X. *Nano Lett.* **2002**, *2*, 1027-1030.

(2) Li, J. J.; Wang, Y. A.; Guo, W. Z.; Keay, J. C.; Mishima, T. D.; Johnson, M. B.; Peng, X. G. *Journal of the American Chemical Society* **2003**, *125*, 12567-12575.

(3) Yu, P. Y.; Cardona, M. *Fundamentals of semiconductors: physics and materials properties*; Springer Berlin etc, 1999.