Predicting the Rate Constant of Electron Tunneling Reactions at the CdSe-TiO_2 Interface

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Table S1: Average lifetime, k_{et} values and errors resultant from the experimental electron transfer studies.			
	<τ> s	k_{et} (s^{-1})	Error
MAA	1.71×10^{-10}	2.34×10^{9}	4.53×10^{7}
3-MPA	1.88×10^{-10}	1.84×10^{9}	4.34×10^{7}
8-MOA	2.12×10^{-10}	1.19×10^{9}	4.38×10^{7}
16-MHA	2.70×10^{-10}	4.92×10^{8}	3.03×10^{7}
SiO_2-MPS	2.87×10^{-10}	N/A	N/A

Table S2: Calculation of Simmons barrier height from the curves shown in Figure S1.			
	Integrated Area (Å*eV)	Width (Å)	φ_{Avg} (eV)
8-MOA	3.8	8.1	0.46
16-MHA	11.1	18.2	0.61

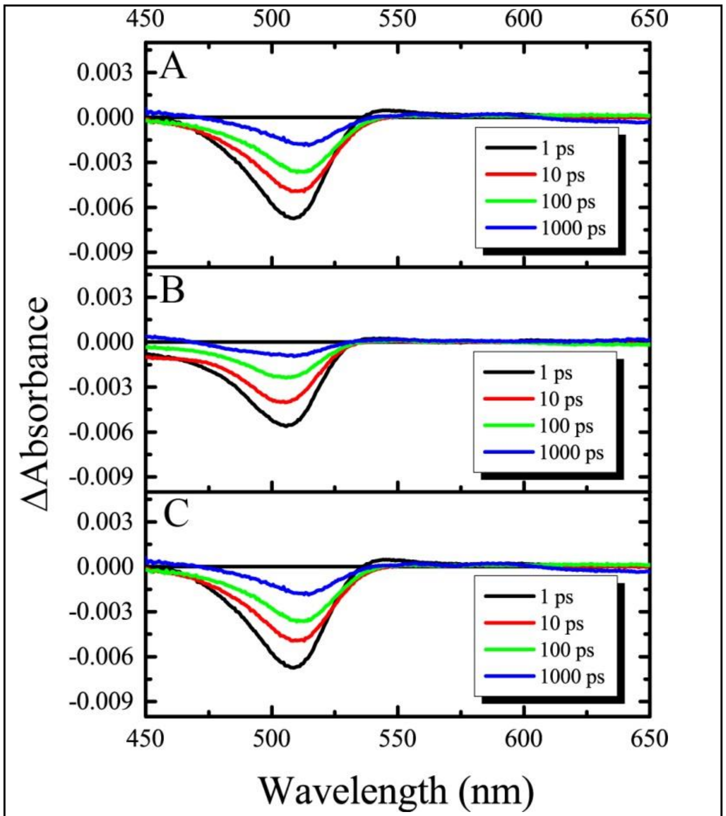

Figure S1: Transient absorption spectra for CdSe-TiO_2 films linked with A) MAA, B) 3-MPA and C) 8-MOA. Each film has a similar ΔAbs magnitude (excited with 1 μJ/pulse at 387 nm) which indicates that the films have comparable QD loading.

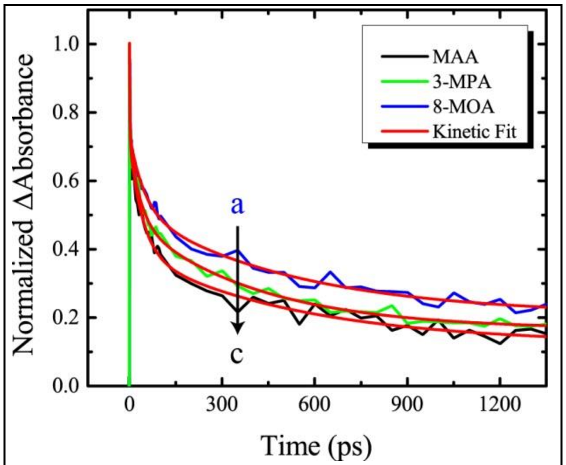

Figure S2: Representative kinetic traces for QDs linked to TiO_2 with a) MOA, b) 3-MPA and c) 8-MOA. The red trace represents the tri-exponential fit of each function.

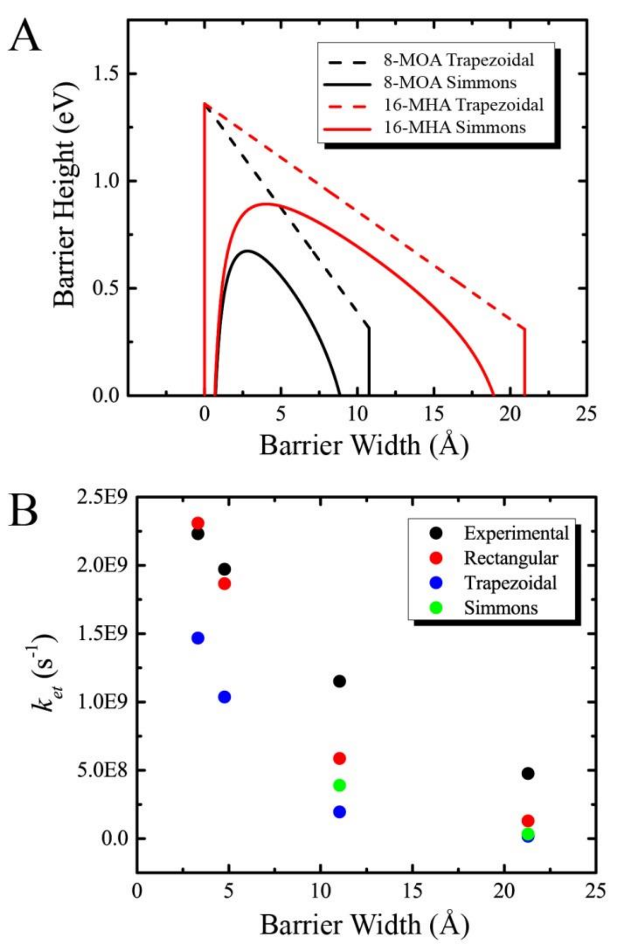

Figure S3: A) Prediction of barrier shape using the Simmons model. B) Calculated values for k_{et} using the average barrier height determined with the Simmons model. Note that the model predicts essentially 0 barrier to electron transfer in the cases of both MAA and 3-MPA.

Simmons Barrier

As discussed in the main text, the Simmons model builds upon the trapezoidal model by reducing the overall height and width of the barrier to account for the coupling of electronic states between donor/acceptor and the organic ligand. This model takes an anti-symmetric hyperbolic shape to allow for the difference between the Fermi levels of CdSe and TiO_2. Employing this model, we see no substantial improvement on the k_{et} values predicted by the trapezoidal approximation. For a more in depth look at the Simmons model please see references 25, 55, 60 and 66 from the main text.