Supplementary Information For

"Effect of Mn dopant on the electron injection in CdSe/TiO$_2$ quantum dot sensitized solar cells"

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The applicability of Marcus-Levich-Dogonadze expression

The Marcus-Levich-Dogonadze expression employed in present work is based on semiclassical Marcus theory, in which the electron transition is treated with a quantum method and the nuclear motion as a classical method. The nuclear relaxation following the electron transfer involves mostly intra-molecular (high-frequency) modes.[1] The Marcus-Levich-Jortner equation is then derived to consider the effect of the quantum vibrational modes in an effective way of

$$k = \frac{2\pi}{\hbar} |V|^2 \frac{1}{\sqrt{4\pi\lambda_{ext}k_B T}} \sum_\nu \exp\left(-S_{eff}\right) \frac{(S_{eff})}{\nu!} \exp\left(-\frac{(\lambda_{ext} + \nu\hbar\omega_{eff} + \Delta G)^2}{4\pi\lambda_{ext}k_B T}\right) \quad (1)$$

where λ_{ext} is the external reorganization energy, S_{eff} is the effective Huang-Rhys factor, and ω_{eff} is the frequency of one effective mode that incorporates in an average way the effect of all quantum modes.[1] The internal reorganization energy λ_{int} does not enter explicitly in Eq. (1), but it is inferred as the sum of contribution from each mode i as follows:

$$\lambda_{int} = \sum_i S_i \hbar \omega_i \quad (2)$$

S_i is the Huang-Rhys factor of the corresponding frequency mode (with frequency ω_i, the summation of i runs over all vibronic modes). λ_{int} is involved in S_{eff} by

$$S_{eff} = \frac{\lambda_{int}}{\hbar\omega_{eff}} \quad (3)$$

To evaluate how the internal reorganization energy is distributed along the various normal modes of the QD (the reorganization energies of TiO_2 substrate are small and ignorable), we computed the individual components of the reorganization energy (to see Eq. 2). Fig. S1 presents the $S_i\hbar\omega_i$ and S_i values at corresponding $\hbar\omega_i$. It is worth noting that the λ_{int} (0.081eV) calculated by canonical mode is not exactly equal to λ_{QD} (0.073 eV) calculated by potential energy surface because the harmonic potential is only an approximation to the actual potential surface. Compared with organic molecule, the vibrational frequencies of QD are much small (within 250 cm^{-1}) due to the heavy elements Cd and Se in the studied structures. The vibrational frequency of 99 cm^{-1} is the main and strongest quantum mode contributing to λ_{int}, so the effective frequency ω_{eff} is set to be 99 cm^{-1} and the corresponding S_{eff} is 6.6, which satisfies the high temperature approximation [$k_B T \geq \hbar\omega_{eff}$ (T=300K)] of semiclassic Marcus theory.[2, 3]
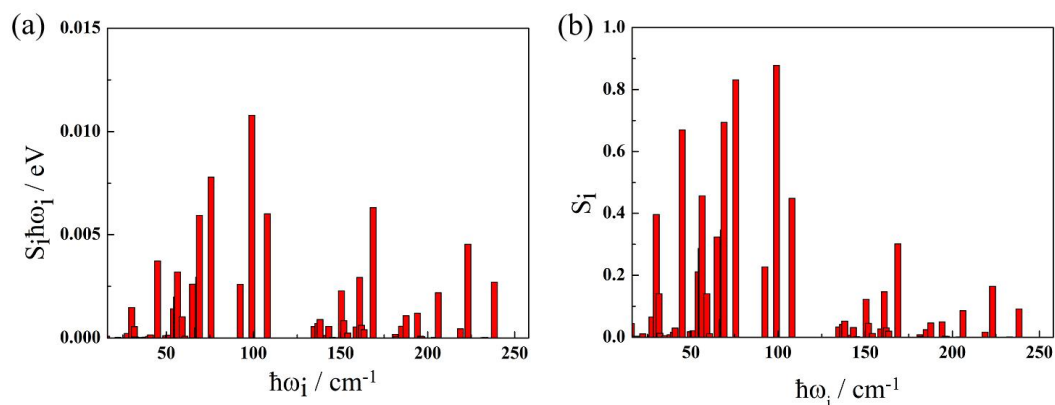
Fig. S1 Distribution of $S_i\hbar\omega_i$ (a) and S_i (b) at different vibrionic modes $\hbar\omega_i$ in $(CdSe)_{13}$.
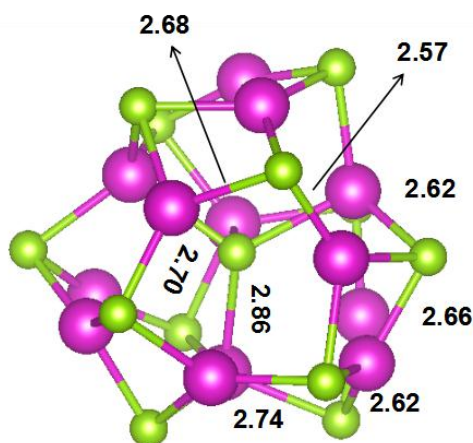

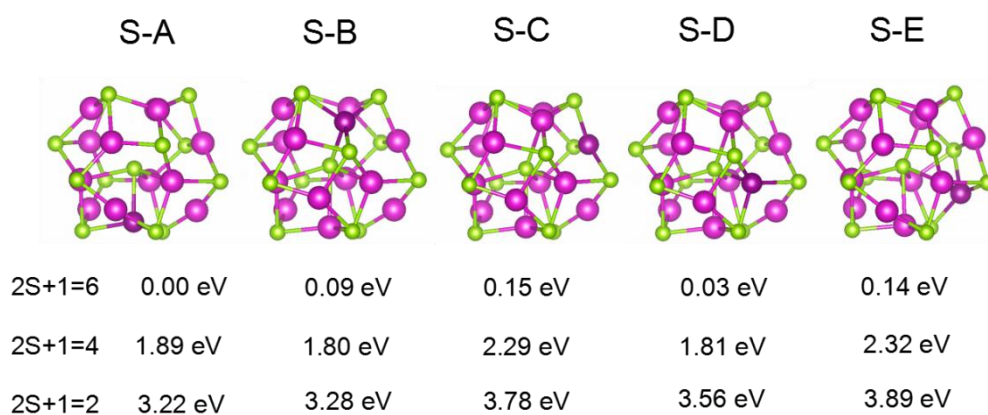**Fig. S2** Selected Cd–Se bond-lengths in $(CdSe)_{13}$ cluster.

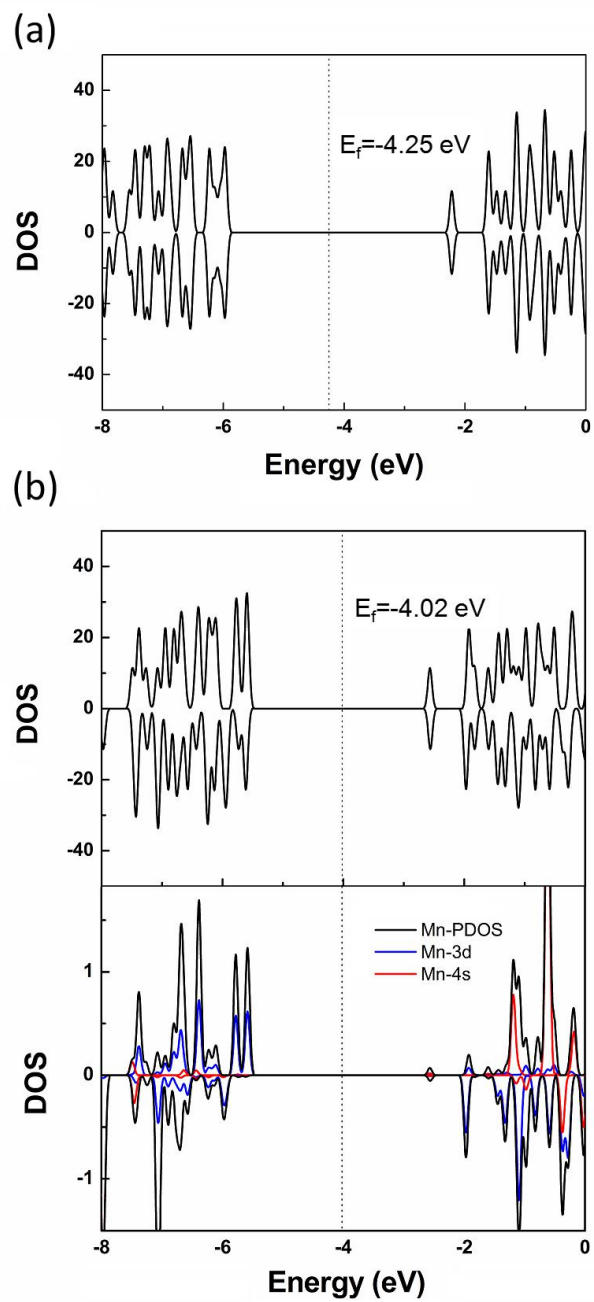|	S-A	S-B	S-C	S-D	S-E
2S+1=6	0.00 eV	0.09 eV	0.15 eV	0.03 eV	0.14 eV
2S+1=4	1.89 eV	1.80 eV	2.29 eV	1.81 eV	2.32 eV
2S+1=2	3.22 eV	3.28 eV	3.78 eV	3.56 eV	3.89 eV

Fig. S3 Structures and energetics of selected low-lying isomers

Fig. S4 Total DOS for (CdSe)$_{13}$ (a) and Cd$_{12}$MnSe$_{13}$ [top of (b)] clusters. PDOS of Mn is presented in the bottom of (b).

ΔE=0.03 eV　　　　ΔE=0.11 eV　　　　ΔE=0.12 eV

ΔE=0.17 eV　　　　ΔE=0.18 eV　　　　ΔE=0.19 eV

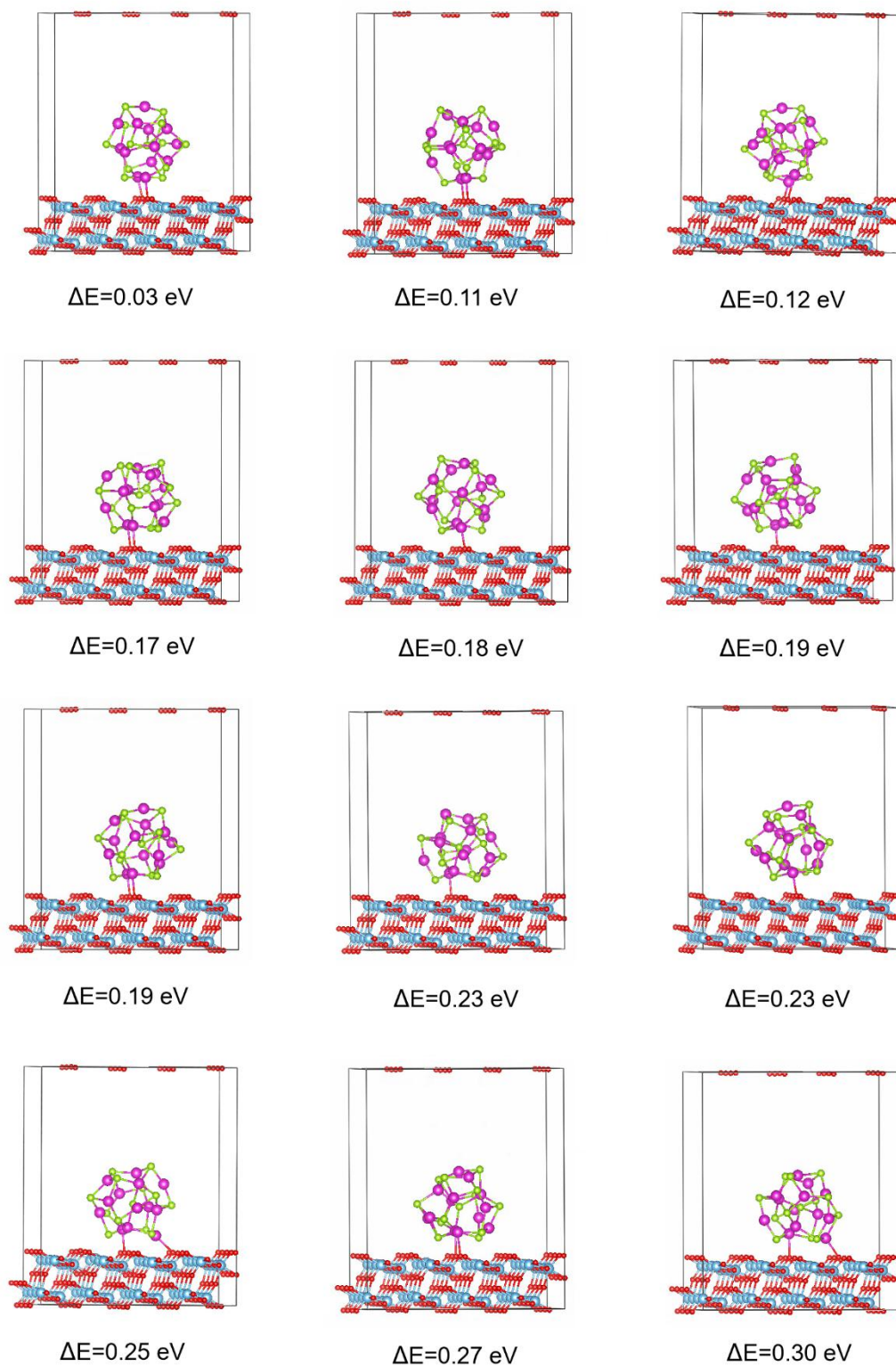ΔE=0.19 eV　　　　ΔE=0.23 eV　　　　ΔE=0.23 eV

ΔE=0.25 eV　　　　ΔE=0.27 eV　　　　ΔE=0.30 eV

Fig. S5 Selected low-lying structures and its relative energy to the lowest energy structure.
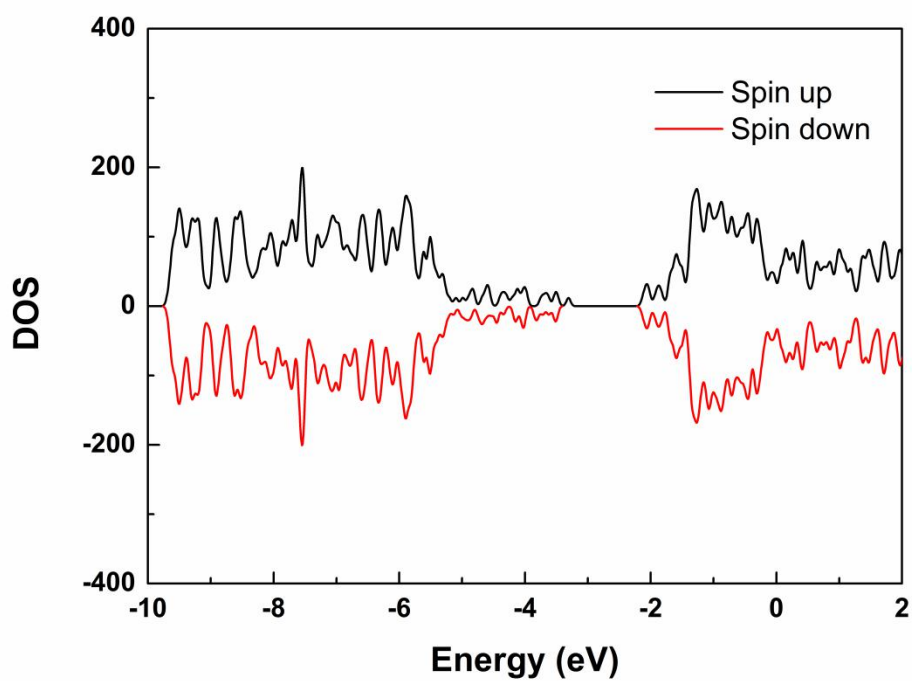
Fig. S6 The spin up and spin down DOS of $Cd_{12}MnSe_{13}@TiO_2$

References

1. T. Liu and A. Troisi, *J. Phys. Chem. C,* 2011**, 115**, 2406-2415.

2. T. Unger, S. Wedler, F.-J. Kahle, U. Scherf, H. Bässler and A. Köhler, *J. Phys. Chem. C,* 2017**, 121**, 22739-22752.

3. E. Lee, E. S. Medvedev and A. A. Stuchebrukhov, *J. Chem. Phys.,* 2000**, 112**, 9015-9024.