Electronic supplementary information for

Novel bifunctional aromatic linker utilized in CdSe quantum dots sensitized solar cell: boosting the open-circuit voltage and electron injection

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The binding modes

The linker adsorption on TiO₂

For considered linkers adsorbed on TiO₂ substrate (here we take PDTCA as example), the end of -COOH binds selectively to the TiO₂ substrate based on experimental report. And the three general adsorption modes (monodentate/hydrogenbond (Mha), bidentate bridging (BB), and bidentate chelating (BC)^{1, 2}) were considered to determine the most stable one based on the equation of adsorption energy $E_{ads}=E_{Substrate/Linker}-E_{Substrate}-E_{Linker}$ (the three items for energies contribute to the total complex, the bare TiO₂, and the isolated linker, respectively). According to our calculation, the BB mode presents the most stable adsorption with the E_{ads} of -4.45 eV among the considered modes, thus, we will use this mode during the whole simulation.



Fig. S1 The binding modes and binding energy of linker on TiO_2 substrate: (a) monodentate/Hydrogen-bond (Mha), (b) bidentate bridging (BB), and (c) bidentate chelating (BC), respectively.

The linker adsorption on CdSe QDs

As for linker capped on CdSe QDs, previous study has indicated that the linker containing -NHCSSH can bind preferentially to the surface Cd atom,³ and there are more than one kind of adsorption mode, e.g., the bidentate bridging (BB), bidentate chelating (BC), chelating tilted (CT), and monodentate bridged (MB) (Fig. S2).^{4, 5} For -CSSH bearing PDTCA, we considered the former three modes where the -CSSH binds to the Cd-rich facet (Fig. 1 (a)), as for -SH bearing MBzA, the last mode was considered. After optimization, we find that all the binding modes for PDTCA transfer to the BB mode, showing that the BB mode is preferable for PDTCA adsorption, so we use this mode for the whole calculations.

It is noted that all linkers are deprotonated after adsorption where the H atoms in - COOH and -CSSH (-SH) transfer to the under-coordination O atom on the surface of TiO_2 and Se atom on the surface of CdSe QDs, respectively.



Fig. S2 The binding modes of linker on CdSe QDs: (a) bidentate bridging (BB), (b) bidentate chelating (BC), (c) chelating tilted (CT), and (d) monodentate bridged (MB), respectively.





Fig. S3 The total density of states (DOS, the gray dot lines) and projected density of states (PDOS, the pink solid lines) of CdSe QDs in the bare structure and abstracted from the complexes with variation of functional groups on the P1 site of PDTCA, and the coupling elements between linkers and QDs in occupied states (the blue lines) and unoccupied states (the orange lines).





Fig. S4 The total density of states (DOS, the gray dot lines) and projected density of states (PDOS, the pink solid lines) of CdSe QDs in the bare structure and abstracted from the complexes with variation of functional groups on the P2 site of PDTCA, and the coupling elements between linkers and QDs in occupied states (the blue lines) and unoccupied states (the orange lines).





Fig. S5 The total density of states (DOS, the gray dot lines) and projected density of states (PDOS, the pink solid lines) of CdSe QDs in the bare structure and abstracted from the complexes with variation of functional groups on the P3 site of PDTCA, and the coupling elements between linkers and QDs in occupied states (the blue lines) and unoccupied states (the orange lines).





Fig. S6 The total density of states (DOS, the gray dot lines) and projected density of states (PDOS, the pink solid lines) of CdSe QDs in the bare structure and abstracted from the complexes with variation of functional groups on the P4 site of PDTCA, and the coupling elements between linkers and QDs in occupied states (the blue lines) and unoccupied states (the orange lines).



Fig. S7 The maximum absorption peak (λ_{max}), transition energy (E_{exc}), and the main contribution associated to the λ_{max} of MBzA/CdSe QDs and PDTCA/CdSe QDs complexes calculated by functional B3LYP and long-range corrected functional CAM-B3LYP combined with the 6-31G(d) (for C, H, O, N, S, F, and Cl atoms) and LANL2DZ (for Se and Cd atoms) basis sets (the isosurfaces are plotted by Gaussian View, isovalue=0.015).



Fig. S8 The simulated absorption spectra by long-range corrected functional CAM-B3LYP: (a) MBzA/QDs (the dash dot line) and PDTCA/QDs (short dash line), (b) R(P1)-PDTCA/QDs, (c) R(P2)-PDTCA/QDs, (d) R(P3)-PDTCA/QDs, and (e) R(P4)-PDTCA/QDs, respectively (the data labeled in all plots present for the maximum absorption peak/transition energies).



Fig. S9 The optimized structures of $TiO_2/linker/CdSe$ QDs heterogeneous (the data labeled in plots are the dihedral angle between NH_2 and NO_2 relative to the benzene ring).

Newns-Anderson model

Take the lowest unoccupied molecular orbital (LUMO) as example, the model can describe the splitting of the LUMO of isolated molecule to a number of mixed levels after adsorption, and the LUMO level energy after adsorption $E_{\text{LUMO}}(\text{ads})$ is assessed by:^{6, 7}

$$E_{\text{LUMO}}(\text{ads}) = \sum_{i} p_i \varepsilon_i \tag{1}$$

where p_i and ε_i are the portion of *i*th molecular orbital (MO) for molecule and its corresponding MO energy, respectively.

For $p_{i,}$ it is calculated by the sum of the squares of the atomic orbital coefficients c_{ij}^{A} that are located on the adsorbed atoms:

$$p_{i} = \frac{\sum_{j}^{A \in \text{Mol}} (c_{ij}^{A})^{2}}{\sum_{j}^{A \in \text{Mol}@Slab} (c_{ij}^{A})^{2}}$$
(2)

Combined with eqn (1) and (2), the mean deviation of the molecular LUMO (electronic coupling element⁸) is defined as follows:

$$\hbar\Gamma = \sum_{i} p_{i} \left| \varepsilon_{i} - E_{\text{LUMO}}(\text{ads}) \right|$$
(3)

Notes and references

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