Validity of density-functional-theory-based molecular modeling for UV/visible spectroscopy and rationale of panchromatic Pbl64−(MeNH3+)4-structured molecular solar cells

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Density-functional-theory-based molecular modeling verifies that perovskite solar cells (PSC) are composed of semiconductor and panchromatic layers constructed by van der Waals and Coulomb interactions (vdW&Clmb) between PbI64−(MeNH3+)4-derived species. Firstly we validate that DFT-based UV/vis spectral analysis is a useful approach for vdW&Clmb based on assignments of the fine-structured UV/vis spectrum of a benzene solution. The UV/vis spectral analysis of aggregated PbI64−(MeNH3+)4 proves that dimeric aggregates of [PbI64−(MeNH3+)4]2 have a panchromatic UV/vis spectrum of a max ranging from 417 to 959 nm. Further analysis proves that the strong vdW&Clmb of PbI64−(MeNH3+)4 leads to unidirectional electron transport at the structured components such as the dimer of [PbI64−(MeNH3+)4]2, nc-TiO2/PbI64−(MeNH3+)4, and PbI64−(MeNH3+)4/spiro-OMeTAD. PbI64−(MeNH3+)4-structured solar cells should have a photoelectron diffusion length enhanced by the alignment of the frontier molecular orbitals in the structured PbI64−(MeNH3+)4 components, which supports remarkable short-circuit photocurrent, open-circuit voltage, and fill factor for the molecular-orbital-connected solar cell of HOTiO23H/[PbI64−(MeNH3+)4]/spiro-OMeTAD under solar-light irradiance.

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1. Introduction

Density-functional-theory (DFT)-based molecular modeling is a novel approach for verifying and predicting the molecular-orbital-based electronic properties of molecular aggregates in which the constituent molecules are aligned by van der Waals and Coulomb interactions (vdW&Clmb).3−5 Recently, Persson and colleagues reported that DFT-based molecular modeling is a useful tool for predicting the electronic and energetic properties of crystalline materials in which crystalline structures play decisive roles in functionalities such as solar light conversion efficiency.6

Molecules in crystalline lattice matrixes are aligned via vdW&Clmb. VdW&Clmb gives rise to London dispersion forces (<1−15 kcal/mol), dipole−dipole interactions (0.5–2 kcal/mol), and hydrogen bonding (1−12 kcal/mol). Molecules and ions have a tendency to form molecular aggregates with various sizes in the quasi-solid states. An accurate prediction of the geometrical configurations in molecular solids and aggregates is required. There have been theoretical investigations on the impact of the geometries on the electronic states by taking into account the intermolecular vdW interaction. The non-empirical or ab-initio vdW-inclusive methods played important roles in predicting the atomic configurations of organic single crystals or organic−metal interfaces, which contributed to the understanding of the geometrical factors dominating electronic properties.3−11 However, the computational complexity or cost of the non-empirical or ab-initio vdW-inclusive methods prevents one from theoretically investigating the electronic properties of realistic molecular aggregates that are of interest from the materials point of view.11 In this work, to gain insights on the material properties, we employ the molecular mechanics optimization of the geometrical configurations taking vdW&Clmb into account, followed by the single-point electronic structure calculation within DFT.

The DFT calculation gives us useful information on molecular aggregates formed by vdW&Clmb, i.e., three-dimensional geometrical configurations, their formation thermodynamics, molecular orbital configurations, surface electron density, and electronic energy structures. The DFT-based molecular modeling of the aggregates enables us to predict theoretical electromagnetic energy spectral data such as UV/vis, IR, FIR, and NMR spectral data.

For UV/vis spectral data, their absorption strength, molecular orbital components, and contribution to respective absorption peaks are extracted. UV/vis spectroscopy simulation with the time-dependent DFT13,14 is likely to be more successful in anticipating changes in color resulting from changes in structure.15 We previously reported that the slip-stacked zinc-phthalocyanine causes a redshift of the calculated and experimental UV/vis spectra.16

Before verifying the panchromatic color of so-called perovskite solar cells, we successfully attempt to validate the fact that the DFT-based modeling of molecular aggregates is useful for verifying and predicting the UV/vis absorption spectra of molecular vdW&Clmb aggregates. We first report that the DFT-based modeling of the vdW&Clmb aggregation of benzene verifies no large difference in calculated and experimental UV/vis spectra of a benzene solution. Secondly, we attempt DFT-based modeling of PbI64−(MeNH3+)4 and its vdW&Clmb aggregates to gain physicochemical insights on the high solar light harvesting efficiency of “so-called” perovskite solar cells (PSC), i.e., panchromatic color and electron diffusion length. The diffusion length of solar cells is defined by the electron lifetime and
electron diffusion coefficient of the solar cell devices being affected by electron leakage at molecular heterojunctions. In the preceding paper, we successfully attempted to verify the high efficiency of PbI$_6^{4-}$-based PSCs by the DFT-based modeling using PbI$_6^{4-}$ in the X-ray crystalline structure, which is denoted as FOLLIB in Cambridge Structural Data (CSD). However, FOLLIB-PbI$_6^{4-}$ was found to be unsymmetrical in P–I bonds, giving unfavourable calculated UV spectra, i.e., $\lambda_{\text{max}} = 261\, \text{nm}$ for FOLLIB-PbI$_6^{4-}$ and $\lambda_{\text{max}} = 280\, \text{nm}$ for [FOLLIB-PbI$_6^{4-}$ (MeNH$_3$)$_4$]$^+$. We carry out DFT-based calculation for the geometrical configurations with symmetrical PbI$_6^{4-}$, and successfully verify that PbI$_6^{4-}$ (MeNH$_3$)$_4$-structured molecular solar cells can be energized by panchromatic solar light energy, collecting photoelectrons effectively with the most suitable diffusion length larger than the component thickness between the electrodes of PbI$_6^{4-}$ (MeNH$_3$)$_4$-aligned solar cells.

2. Theoretical methods

Single-point DFT calculations were performed using the B3LYP exchange–correlation functional and 6-31G(d) basis set with Spartan. Prior to the single-point DFT calculation for electronic properties, the geometries of the molecular aggregates were determined by the molecular mechanics simulation employing the Merck Molecular Force Field (MMFF). The validity of the geometrical configurations of the molecular aggregates was confirmed by the single-point total energy calculation at the B3LYP-D3 level of theory. The basis set superposition error was eliminated by using the counterpoise correction.

The configurations of the molecular orbitals for vdW&Clmb molecular aggregates, molecular aggregation energy ($\Delta E$), dipole moment, and energy of the molecular orbitals such as LUMO (ELUMO), HOMO (EHOMO), and LUMO+1 (ELUMO+1) are obtained as key data. Here, the results are based on the single-point B3LYP/6-31G(d) calculation. It is found that the results obtained with B3LYP-D3/def2-QZVP do not change the conclusion. The electron transfer gaps $\Delta E_t$ (ELUMO–EHOMO) and $\Delta E_t$ (ELUMO (−1)–ELUMO) are measures of the semiconductor electron transfer capability at the ground and excited states (electron accepted states, i.e., radical anion states) of molecules and molecular aggregates. The chemical reactivities of the molecular species have been successfully investigated in terms of the change in electron density of the frontier orbitals upon electron addition/extraction, i.e., the Fukui function. The semiconducting carrier mobility or electrical conductivity of the PSC materials has been reported. For UV/vis analysis revealing the allowed transitions between molecular orbitals with wavelength and intensity, the timedependent DFT within the linear response regime was used. The surface electron density and electrostatic potential map are used for understanding the vdW&Clmb aggregation as a new type of molecule without covalent bonding. For a review of the quantum mechanical methods used in Spartan, see Ref. 36.

3. Results and discussion

3.1 vdW&Clmb aggregation of benzene molecules

The DFT electronic structure calculation of the packing unit of benzene crystals denoted by BENZEN18 in CSD, i.e., (C$_6$H$_3$)$_{14}$, single benzene (C$_6$H$_6$ BENZEN18), and orthogonal benzene dimer [(C$_6$H$_3$)$_2$ BENZEN18] was carried out to obtain both molecular orbital structures and UV/vis spectra, which are all single-point energy-based calculations (SPE) (Figs. S1-1, S1-2, S2-1, S2-3, S3-1, and S3-3 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia). The DFT calculation of single benzene (C$_6$H$_6$) and MMFF-optimized benzene dimers of oblique (C$_6$H$_6$)$_2$ and orthogonal (C$_6$H$_6$)$_2$ is performed for respective single-point energy-based (SPE) and equilibrium geometry-based (EQG) structures (Table S1, Figs. S2-2, S2-3, S3-2, S4-1, and S4-2 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia).

The SPE-based oblique (C$_6$H$_6$)$_2$ configuration, the most stable dimer configuration in this study, gives $\Delta E$ of −1.97 eV, which is lower than that of the orthogonal dimer by 0.3 eV. Given the previous theoretical studies reporting lower $\Delta E$ by using accurate wave function-based or the non-local vdW-inclusive density functional method, we might expect other configurations with lower $\Delta E$. However, in this study, we focus on the electronic properties of the molecular aggregates in crystal matrices or in solutions, rather than the detailed geometrical configurations of an isolated dimer.

The benzene trimer (C$_6$H$_5$)$_3$ is investigated with DFT for SPE and EQG geometries obtained with the MMFF-based optimization of the oblique-oriented (C$_6$H$_5$)$_3$ structure. The EQG-based structure is confirmed to give a higher exothermic formation energy than the SPE-based oblique dimer, and its molecular orbital energetics and UV/vis spectrum are shown in Figs. S5-1 and S5-2 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia.

As for the benzene tetramer from the EQG-based oblique (C$_6$H$_5$)$_4$, one benzene molecule is placed orthogonally to the oblique-oriented trimer of (C$_6$H$_5$)$_3$, being optimized by MMFF, and the trimer-derived (C$_6$H$_5$)$_3$ is determined as the metastable EQG structure (Figs. S6-1 and S6-3 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia). We expected the benzene tetramer as a dimer of the EQG-based orthogonal (C$_6$H$_5$)$_2$, considering that the orthogonal (C$_6$H$_5$)$_2$ has the molecular orbital with degenerated HOMO and LUMO, as is the case of a single benzene molecule to form an orthogonal (C$_6$H$_5$)$_2$ (Figs. S2-2 and S3-2 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia). The tetramer (C$_6$H$_5$)$_4$ from a dimeric aggregate of the orthogonal dimer of (C$_6$H$_5$)$_2$ is found to be most stable, and the UV/vis spectra are obtained (Figs. S6-2 and S6-3 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia).

As for a pentamer of (C$_6$H$_5$)$_5$, one benzene molecule is placed orthogonally to the trimer-derived (C$_6$H$_5$)$_3$, being optimized by MMFF, and the UV/vis spectrum is determined (Figs. S7-1 and S7-2 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia).

As for two kinds of (C$_6$H$_5$)$_6$, hexamer-1 of (C$_6$H$_5$)$_6$ (tall) and hexamer-2 of (C$_6$H$_5$)$_6$ (compact) are molecular-modeled as dimers of (C$_6$H$_5$)$_2$, considering that the oblique-oriented (C$_6$H$_5$)$_2$ has the molecular orbital with degenerated HOMO and LUMO. Hexamer-2 of (C$_6$H$_5$)$_6$ (compact) is found to be metastable, whose aggregation energy of $\Delta E = −12.4$
kcal/mol is higher by 1.7 kcal/mol than that of hexamer-1 ($\text{C}_6\text{H}_6\text{}_6$ (tall)). In addition, hexamer-2 gives the longest $\lambda_{\text{max}} = 230 \text{ nm}$ with the smaller energy transfer gap of $\Delta E_t = 6.25 \text{ eV}$. The electron density and electrostatic potential map indicate a more compact benzene alignment than that of hexamer-1 (Figs. S8-1, S8-2, and S8-3 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia).

### 3.2 Validity of density-functional-theory-based molecular modeling for UV/vis spectra of molecular aggregates

The examination of UV/vis spectra of benzene reveals that the thin film of a benzene solution (4 °C) has a structured UV absorption in the range of $\lambda = 200$–210 nm and the benzene solution has a very weak but fine-structured UV absorption in the range from $\lambda = 225$ to 270 nm. On the other hand, the crystalline structure of benzene was determined by X-ray crystallography (BENZEN18 in CSD[37]). Interestingly, the packing unit consists of 7 orthogonal benzene dimers [totally, 14 benzene molecules of ($\text{C}_6\text{H}_6$)$_{14}$]. We understand that benzene molecules aggregate with each other orthogonally via vdW&Clmb.

DFT single-point calculations of a benzene single molecule and the orthogonal benzene dimer in BENZEN18 give almost the same molecular orbital structures as the EQG-based benzene and the EQG-based orthogonal benzene dimer (Figs. S2-1, S2-2, S3-1, and S3-2 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia). The DFT-based UV/vis spectrum of the packing unit in BENZEN18 gives very weak absorptions in the range of 219–220 nm, and the calculated UV/vis spectra of the EQG-based $\text{C}_6\text{H}_6$ (EQG-$\text{C}_6\text{H}_6$) and the EQG-based orthogonal benzene dimer of EQG-($\text{C}_6\text{H}_6$)$_2$ give UV/vis spectra comparable to the experimental one (Figs. S2-3, S3-3 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia, and Fig. 1). The benzene ring structure of EQG-based $\text{C}_6\text{H}_6$ is almost comparable to that in BENZEN18 as shown in Fig. 1, but the distance between the benzene rings is closer in the orthogonal benzene dimer in BENZEN18 than in the EQG-based orthogonal benzene dimer. Crystal matrixes make the distance closer, and such aggregation never affects the UV/vis spectra in solution.

Further vdW&Clmb aggregations of benzene, i.e., SPE-based oblique dimer ($\text{C}_6\text{H}_6\text{}_2$), EQG-based oblique trimer ($\text{C}_6\text{H}_6\text{}_3$), trimer-derived tetramer ($\text{C}_6\text{H}_6\text{}_4$), and tetramer ($\text{C}_6\text{H}_6\text{}_4$) as a dimer of orthogonal dimer, are molecular-modeled. The UV/vis spectra are shown in Fig. 2, along with their density structures. For comparison with the experi-
mental UV/vis spectra of vapor benzene, those of a thin amorphous state of benzene at 4.2 K were shown (Fig. 2).

The strong absorption of vapor in the range between 170 and 190 nm is explained as due to a single benzene molecule, and the fine structured absorption of film-like solid benzene at 4.2 K as due to the amorphous state of mixtures consisting of at least dimers, a trimer, tetramers, a pentamer, and two kinds of hexamers of benzene aggregates. Agreement of the theoretical absorption spectra obtained at the TDDFT/B3LYP level of theory with experiments implies that the excited states of interest are dominated by the intramolecular valence excitations of a single benzene molecule, which are more or less perturbed by the molecular aggregation.

The DFT-based UV/vis spectra of pentamer (C\textsubscript{6}H\textsubscript{6})\textsubscript{5} and hexamer-1 and hexamer-2 of (C\textsubscript{6}H\textsubscript{6})\textsubscript{6} are shown in Fig. 3 with very weak structured absorption in the range of 220–270 nm. The DFT-based UV/vis absorption in the range of 224–230 nm appears even in the EQG-based single benzene, and the intensity increases with the number of aggregating benzene molecules. The metastable compact hexamer-2 gives the maximum UV/vis absorption at 230–231 nm. A benzene solution is a mixture of the vDW&Clmb aggregation of benzene molecules. The metastable compact hexamer-2 gives the maximum UV/vis absorption at 230–231 nm. The DFT-based UV/vis spectra of pentamer (C\textsubscript{6}H\textsubscript{6})\textsubscript{5} and benzene hexamer-1 and hexamer-2 of (C\textsubscript{6}H\textsubscript{6})\textsubscript{6} as dimers of the EQG-based oblique trimer (C\textsubscript{6}H\textsubscript{6})\textsubscript{3}

3.3 DFT-based simulation for vDW&Clmb aggregation of PbI\textsubscript{6}+&\{(MeNH\textsubscript{3})\textsuperscript{+}\}4

The DFT-based electronic structure of PbI\textsubscript{6}+ is determined by EQG-based calculations of MMFF-optimized PbI\textsubscript{6}+. The DFT-based calculation for the vDW&Clmb aggregation of PbI\textsubscript{6}+&\{(MeNH\textsubscript{3})\textsuperscript{+}\}4 is carried out using the coded EQG-based PbI\textsubscript{6}+, in which the P–I bond is frozen (Table S2 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia and Fig. 4).

The electronic structure simulation of [PbI\textsubscript{6}+&\{(MeNH\textsubscript{3})\textsuperscript{+}\}1\textsubscript{0}]\textsuperscript{0} is as follows. Successive calculations for equilibrium geometric structures of [PbI\textsubscript{6}+&\{(MeNH\textsubscript{3})\textsuperscript{+}\}]\textsuperscript{3}, [PbI\textsubscript{6}+&\{(MeNH\textsubscript{3})\textsuperscript{+}\}]\textsuperscript{2} and [PbI\textsubscript{6}+&\{(MeNH\textsubscript{3})\textsuperscript{+}\}]\textsuperscript{1} are conducted for MMFF-optimized structures. As for [PbI\textsubscript{6}+&\{(MeNH\textsubscript{3})\textsuperscript{+}\}]\textsuperscript{2}, MeNH\textsubscript{3}+ is placed on the last MeNH\textsubscript{3}+-free corner in EQG-based [PbI\textsubscript{6}+&\{(MeNH\textsubscript{3})\textsuperscript{+}\}]\textsuperscript{1} as a symmetrical structure of EQG(1)-[PbI\textsubscript{6}+&\{(MeNH\textsubscript{3})\textsuperscript{+}\}]\textsuperscript{1} and calculated for equilibrium geometry without MMFF optimization (Fig. S9 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia). As for the isomer EQG(2)-[PbI\textsubscript{6}+&\{(MeNH\textsubscript{3})\textsuperscript{+}\}]\textsuperscript{1}, DFT calculation is carried out, followed by MMFF optimization (Fig. S10 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia). The calculation using FOLLIB-based PbI\textsubscript{6}+&\{(MeNH\textsubscript{3})\textsuperscript{+}\}4 is carried out as well, and the molecular orbital structures are obtained for comparison (Fig. S11 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia).

As for the vDW&Clmb self-aggregation of PbI\textsubscript{6}+&\{(MeNH\textsubscript{3})\textsuperscript{+}\}4 and PbI\textsubscript{6}+ units are allowed to interact with each other symmetrically with the inter-unit distances of 3.603 and 3.609 Å, and the resulting aggregate structure is molecular-modeled for SPE-based [PbI\textsubscript{6}+&\{(MeNH\textsubscript{3})\textsuperscript{+}\}]\textsubscript{2} (Fig. 5 and Fig. S12 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia) and EQG(1)-[PbI\textsubscript{6}+&\{(MeNH\textsubscript{3})\textsuperscript{+}\}]\textsubscript{2} (Fig. 5 and Fig. S13 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia).
supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia). EQG(2)-[Pbl64+(MeNH3)+]2 is molecular-modeled for the aggregation structure with distances of 3.995 and 3.934 Å (Fig. 5 and Fig. S14 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia). It is worth noting that the exothermic formation energy (ΔE) with B3LYP/6-31G(d) is very large (~1192, ~1546, and ~1551 kcal/mol), compared with the vdW&Clmb aggregation of benzene molecules, implying the large contribution by the electrostatic attraction.

As for the vdW&Clmb alignment of PbI64+(MeNH3)+ on nanocrystalline anatase TiO2, the Yamashita and Jono model of HOTiO3SnTi4(41) is introduced. In the HO-free Yamashita–Jono model, [Ti3O8H]+ is allowed to locate symmetrically on EQG(1)-[PbI64+(MeNH3)+] at distances of 4.685 and 2.611 Å (Fig. 6). Introducing the HO− group to the aggregated [Ti3O8H]+, the interfacial structure is successfully molecular-modeled where all MeNH3+ ions are not frozen. It is worth noting that the electron transfer gap between LUMO+1 and LUMO is 0.45 eV, suggesting the formation of semiconducting electronic structures at the interface.

As for the vdW&Clmb alignment of PbI64+(MeNH3)+ on 2,2,7,7-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobi-fluorene (spiro-OMeTAD), the asymmetrically aggregated structure with the distance of Pb–N, 9.519 Å (Fig. 7), is successfully molecular-modeled with ΔE = ~761 kcal/mol. The electron transfer gap between LUMO+1 and LUMO is 0.24 eV, suggesting the formation of semiconducting electronic structures at the interface.

3.4 Rationale of high efficiency of panchromatic Pbl64+(MeNH3)+-structured molecular solar cells

We have found differences in chemical structures between the FOLLIB-based and the DFT-simulation-based PbI64+. Surprisingly, their calculated UV/vis spectra are quite different in absorption maxima and intensity (Fig. 4). While FOLLIB-PbI64+ and FOLLIB-PbI64+(MeNH3)+ (Fig. S11 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia) are calculated to have respective absorption maxima (λ max) at 256 and 280 nm, the DFT-simulation-based PbI64+ and their salts with (MeNH3)+, i.e., [EQG(1)-PbI64+(MeNH3)+]2 and [EQG(2)-PbI64+(MeNH3)+]3 (Fig. S9 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia), are calculated to have the red-shifted λ max at 383, 417, and 513 nm, respectively.

FOLLIB-PbI64+ consists of different Pb–I bond lengths, ranging from 3.195 to 3.765 Å. It is worth noting that the case is true for the orthogonal benzene dimer in BENZEN18. The average dihedral angle ϕ in the shortest separation distance observed between the EQG-based orthogonal benzene dimer and the one in BENZEN18 is calculated to be 0.518 Å (Fig. 1). The structural change may come from a kind of strain caused by crystalline matrices. Considering that there is no such strain at amorphous states, the three-dimensional symmetrical structure of EQG(1)-PbI64+(MeNH3)+ is chosen for the DFT-simulation-based rationale of the high efficiency of PSC.

Given the vdW&Clmb aggregation as observed in PbI64+ alignments in FOLLIB, we attempt the DFT-based simulation of the vdW&Clmb dimerization of EQG(1)-PbI64+(MeNH3)+. Since EQG(1)-PbI64+(MeNH3)+ has no degenerate molecular orbitals, they are aligned manually with their spatial separation set to the vdW distance, and three kinds of dimer of EQG(1)-PbI64+(MeNH3)+ are molecular-modeled. The vdW&Clmb-based dimers, SPE-based [PbI64+(MeNH3)+]2, EQG(1)-[PbI64+(MeNH3)+]2, and EQG(2)-[PbI64+(MeNH3)+]2 are summarized in Fig. 5 (Figs. S12–S14 in the online supplementary data at http://stacks.iop.org/JJAP/57/121602/mmedia). All UV/vis spectra verify that the panchromatic color of PSC harvests solar light effectively, resulting in a high short-circuit photocurrent in PSC.

As mentioned in the preceding papers, the energy transfer gap between LUMO and LUMO+ is a measure of the semiconducting molecular transfer under solar light irradiance. Photogenerated electrons convert LUMO and LUMO+ into HOMO (SOMO) and LUMO of the resulting radical anion. The energy transfer gap of radical anions of three isomers is in the range of less than 0.2 eV (0.14, 0.19, and 0.05 eV, respectively), verifying that the [PbI64+(MeNH3)+]2-aligned molecular layer becomes semiconducting under photo-energized bias conditions.

In addition, we have predicted and verified the important roles of the semiconducting properties of heterojunction-induced vdW&Clmb in dye-sensitized solar cells and photo-electrochemical water splitting. From these viewpoints, so-called perovskite solar cells should have remark-

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**Fig. 4.** (Color online) Structural and UV/vis spectral comparison of FOLLIB-PbI64+(MeNH3)+ and DFT-based PbI64+(MeNH3)+: [EQG(1)-PbI64+(MeNH3)+]2.
able semiconducting properties, i.e., unidirectional photo-electron flow from [PbI₆⁴⁻(MeNH₃⁺)₄]²⁺ to nc-TiO₂, and from spiro-OMeTAD to [PbI₆⁴⁻(MeNH₃⁺)₄]²⁺ of solar cells consisting of nc-TiO₂= PbI₆⁴⁻&(MeNH₃⁺)₄= spiro-OMeTAD.

As expected from the preceding paper, the interfacial structures of [PbI₆⁴⁻(MeNH₃⁺)₄] and nc-TiO₂ are successfully molecular-modeled using the Yamashita–Jono nc-TiO₂ model, [HOTi₉O₁₈H](PbI₆⁴⁻&(MeNH₃⁺)₄) (Fig. 6). Interestingly, HOMO locates between the HO group on the nc-TiO₂ model and the iodine atom on PbI₆⁴⁻, verifying the interfacial vdw&Clmb interaction. The electron transfer gap of the radical anion of the structure is ~0.45 eV, suggesting unidirectional electron transfer at the interface under photo-energized bias conditions.

The case is also true for the interfacial structure between [PbI₆⁴⁻(MeNH₃⁺)₄] and spiro-OMeTAD. In particular, the electron transfer gap of the radical anion of the structure is estimated to be ~0.24 eV, verifying the unidirectional electron transfer at the interface as well (Fig. 7).

In general, a high open-circuit voltage (V_{oc}) of more than 1 eV is essential for a highly efficient PSC. To verify the facts, the theoretical maximum V_{oc} is calculated from...
the UV/vis allowed transition in the molecular orbital of [PbI$_6^{4-}$](MeNH$_3^+$)$_4$-aligned molecules (Fig. 8).

Assuming that photoelectrons on unoccupied molecular orbitals should transfer to LUMO+1 of HOTi$_9$O$_{18}$H&PbI$_6^{4-}$,(MeNH$_3^+$)$_4$, the maximum $V_{oc}$ is obtainable as electron transfer from the occupied molecular orbitals of panchromatic dimers of [PbI$_6^{4-}$](MeNH$_3^+$)$_4$ to the higher unoccupied molecular orbital of LUMO+1 on nc-TiO$_2$. The panchromatic dimers of EQG(1)-[PbI$_6^{4-}$](MeNH$_3^+$)$_4$ and EQG(2)-[PbI$_6^{4-}$](MeNH$_3^+$)$_4$ give the maximum $V_{oc}$ values of 1.1 and 1.5 eV, respectively.

4. Conclusions

We have shown that the DFT-based calculation can verify and predict the color of molecules in amorphous states, in which they aggregate by vdW&Clmb. On the basis of the DFT-based verification of vdW&Clmb molecular alignments and UV/vis spectroscopy, PSC is now visualized as a one-molecular wire by space-filling-model-based, electrostatic-potential-map-based, and LUMO-chain-based structures (Fig. 9). In other words, PSC can be regarded as a bundle of [PbI$_6^{4-}$](MeNH$_3^+$)$_4$-structured one molecular wires. The
quantum-dot-like or photosynthetic-like molecular structure rationalizes the large photoelectron diffusion length for the high photocurrent ($J_{sc}$), high $V_{oc}$, and respectable fill factor (ff) of the one-molecular-like wire of nc-TiO$_2$/PbI$_6^{4−}$(MeNH$_3$)$_4$/spiro-OMeTAD under solar-light irradiance.

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