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Surface Molecular Doping of All-Inorganic Perovskite Using Zethrenes Molecules

Arramel¹ (✉), Hu Pan², Aozhen Xie^{3,4,5}, Songyan Hou^{3,4}, Xinmao Yin^{1,6}, Chi Sin Tang^{1,6,7}, Nguyen T. Hoa³, Muhammad D. Birowosuto³, Hong Wang^{3,4}, Cuong Dang^{3,5} (✉), Andriwo Rusydi^{1,6,8}, Andrew T. S. Wee^{1,9,10}, and Jishan Wu² (✉)

¹ Department of Physics, National University of Singapore, 2 Science Drive 3, 117542, Singapore

² Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543, Singapore

³ CINTRA UMI CNRS/NTU/THALES 3288, Research Techno Plaza, 50 Nanyang Drive, Level 6, Border X Block, Singapore 637553, Singapore

⁴ School of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

⁵ Energy Research Institute @NTU (ERI@N), Nanyang Technological University, Research Techno Plaza, X-Frontier Block, Level 5, 50 Nanyang Drive 637553, Singapore

⁶ Singapore Synchrotron Light Source, National University of Singapore, 5 Research Link, Singapore 1176033

⁷ NUS Graduate School for Integrative Sciences and Engineering (NGS), National University of Singapore, Singapore 117456

⁸ NUSNNI-NanoCore, National University of Singapore, Singapore 117411

⁹ Institute of Materials Research & Engineering (IMRE), A*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, Innovis, Singapore 138634

¹⁰ Centre for Advanced 2D Materials, National University of Singapore, Block S14, Level 6, 6 Science Drive 2, Singapore 117546

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ABSTRACT

We present an optical and photoelectron spectroscopic study to elucidate the interfacial electronic properties of organic-inorganic semiconductor heterojunctions formed in a kinetically blocked heptazethrene (HZ-TIPS) and its homologue, octazethrene (OZ-TIPS) on an all-inorganic perovskite cesium lead bromide (CsPbBr₃) surface. An interfacial dipole was formed at the interface due to the competing interaction between the dispersion force of the bulky TIPS-substituent group and the attractive van der Waals interaction at the first few layers. Photoemission spectroscopy of the physisorbed HZ-TIPS shows chemical shift, which indicates electron transfer from HZ-TIPS molecules to the CsPbBr₃ perovskite single crystal. In contrast, the adsorbed OZ-TIPS molecular layer on CsPbBr₃ demonstrates the opposite trend indicating a hole transfer process. The average molecular orientation as determined by near edge x-ray absorption fine structure (NEXAFS) suggests that the HZ-TIPS molecular plane is generally lifted with respect to the perovskite surface. We suggest that the nature of the closed-shell electronic ground state of HZ-TIPS could contribute to the formation of interfacial dipole at the molecule/perovskite interface.

1 Introduction

In recent years, all-inorganic cesium lead halide perovskites (CsPbBr₃) have gained a lot of attention and emerged as a promising class of wide band gap semiconductors for diverse electronic applications. Their excellent stability[1], high absorption span up to the visible range[2], size-tunable band gap[3] and efficient narrow-band emission[4] render them as promising next generation material candidates for performance photovoltaic and optoelectronic devices compared to its predecessor hybrid organic-inorganic perovskites[5-8]. Several promising physical properties of the perovskites include their large absorption coefficients, long carrier lifetimes, and balanced hole and electron transport.[9-12] To optimize their potential use, a thoroughly assessment of the electronic structure and the chemical state of perovskite interfaces across the heterojunction device is required. In that regard, well-defined knowledge on the interfacial electronic structure of the constituent organic-inorganic heterointerfaces is needed. Thus, the detailed energy positions of valence band maximum (VBM) and conduction band minimum (CBM), vacuum level (VL), ionization energy (IE) and electron affinity (EA), are of significance not only for controlling molecule/perovskite interfaces but also for optimizing the device efficiency for better performance.

An intriguing class of open-shell π -conjugated poly aromatic hydrocarbon (PAH) organic molecules are the zethrenes which have been studied due to its peculiar molecular and spin structure[13-15]. Due to its stable biradical character, this class of PAHs can be recognized from their z-shaped chemical structure that typically comprises of two phenalene units fused together with C-C double bonds. Thus, two distinctive chemical resonance structures, a closed-shell quinoidal form and an open-shell

biradical form can be realized and this will manifest in diverse optical, magnetic and electronic properties[13, 16, 17]. For example, Li et al.[18] proposed a synthetic pathway for the rational design of kinetically-blocked heptazethrenes triisopropylsilyl ethynylene (HZ-TIPS) derivatives and its homologue octazethrenes (OZ-TIPS) illustrated in Fig. 1a and 1b that have different electronic ground states. The former has a closed-shell ground state while the latter octazethrene analogue possesses an open-shell singlet biradical with smaller optical band gap[18]. To the best of our knowledge, there is no systematic study that has been carried out to investigate the heterointerface interactions between these low-band gap organic materials and the all-inorganic perovskites.

In the past few years, improvements have been made to stabilize the reactive sites and to extend radical character of zethrene molecules[17, 19, 20]. However, work to understand the behavior of the aforementioned molecule on a surface is still lacking, in particular, how the zethrene interacts with the underlying substrate. With regards to its highly reactive nature, Li et al[18] used a passivated TIPS functional group on the zethrene molecular backbone to kinetically-block its reactivity. This introduces geometric non-planarity that can be investigated using angle resolved near edge x-ray absorption fine structure (NEXAFS) spectroscopy. In addition, the peculiar difference between the electronic ground state of OZ-TIPS and HZ-TIPS could be used to tune the interfacial electronic properties of perovskites. Thus, in this scenario, the zethrene molecule serves as weakly physisorbed adlayer dopant that could have practical applications in the fields of optoelectronics, nonlinear optics, spintronics or energy storage.

Surface charge transfer doping using organic molecular layers as an active material on an emergent

Address correspondence to phyarr@nus.edu.sg, HCDang@ntu.edu.sg, chmwuj@nus.edu.sg

subject such as perovskites could play an important role for tuning their optical and electrical properties[21]. Surface transfer doping offers a simple and effective method to manipulate the electronic properties of diverse semiconductor materials. In comparison to the conventional electrostatic modulation via an external electrical field, surface transfer doping typically offers a stronger non-volatile doping performance that is applicable for further device fabrication purpose.

Ultimately, this could potentially widen their control on the majority charge carrier or fine tune their Fermi level position of the aforementioned perovskites. Several studies have been reported on the interfacial interaction between organic molecules on homologue hybrid inorganic-organic perovskites such as the methyl ammonium lead halide (MAPbX₃) family[22–25]. However, there are only a few existing studies[26, 27] that have concentrated an emphasis on molecular doping on the modification of electronic structure of CsPbBr₃ perovskites.

According to the report by Shan et al., the electron mobility of thermally-deposited zethrene as active thin organic film transistor is only 0.05 cm² V⁻¹ S⁻¹[28]. The reported mobility is somewhat smaller in comparison to the other well-developed organic π -conjugated system such as pentacene[29] or rubrene[30]. We therefore seek to shed some light on how one could modulate the charge transfer event at the zethrene/CsPbBr₃ interface by predefining the choice of molecular functionality. The investigation was carried out using combined x-ray and ultraviolet photoemission and near-edge absorption spectroscopy performed at room temperature.

Here we elucidate the evolution of the valence and conduction band levels as functions of zethrenes molecular thicknesses. It turns out that the magnitude of charge transfer rises significantly when CsPbBr₃ was doped by HZ-TIPS molecule. On the contrary, we do not observe this for its homologue, OZ-TIPS. This work suggests that at sub-monolayer coverage of HZ-TIPS, an upward band bending in

combination with the dipole formation was established at the CsPbBr₃/HZ-TIPS interfaces.

2 Experimental

Perovskite single crystal fabrication. All-inorganic perovskite CsPbBr₃ was synthesized as previously reported by Rakita et al.[31] with several modifications. The precursor solution of 0.5 M of CsPbBr₃ was first prepared by dissolving an equimolar amount of PbBr₂ and CsBr in DMSO at 50 °C for 2h. The solution was then saturated by adding an appropriate amount of methanol (DMSO/CH₃OH = 1/0.55 by volume) at room temperature. Subsequently, the saturated solution was heated at 50 °C for 24h followed by heating at 80 °C for 8h. The precursor was filtered (0.2 μ m PTFE) and placed in a vial. The vial was kept undisturbed with temperature increasing gradually from room temperature to 80 °C for crystal growth. The crystals were collected and stored in DMF for further use.

XRD measurements. High resolution x-ray diffractometry characterization for the hybrid halide perovskite crystal samples were conducted at the X-ray Demonstration and Development (XDD) beamline at the Singapore Synchrotron Light Source (SSLS). All diffraction measurements were performed at room temperature. Data acquisition of the x-ray diffractograms is carried out in two-axis mode with a step size of 0.02° over a Bragg angle range of 10–80°.

SEM measurements. SEM micrographs were taken under 6 kV accelerating voltage in secondary electron mode using JEOL JSM-5600LV system.

AFM inspection. The morphology of as-synthesized CsPbBr₃ was characterized using a commercial atomic force microscope (AFM, BRUKER Dimension FastScan). A standard cantilever with spring constant of 40 N/m and tip curvature <10 nm was used as the probe.

Photoluminescence measurements. Room temperature Photoluminescence (PL) measurements were performed using free space excitation and collection through a visible–near infrared microscope objective (Nikon 20×, NA = 0.40). The samples were excited with a ps-pulsed ytterbium fiber laser emitting at high harmonic generation of 266 ± 1 nm wavelength with 10 MHz repetition rate, focused to a spot size of less than $1\mu\text{m}$. Photoluminescence was detected using a Peltier-cooled photomultiplier tube (Hamamatsu H7422 series) coupled to a grating spectrometer (Edinburgh Instruments F900 and Bentham TMS300). Time-resolved decay traces were acquired by a time-correlated single photon counting acquisition module (Edinburgh Instruments, TCC900) at selected wavelength of 534 ± 5 nm.

Raman measurements. Raman spectra were collected using a 532 nm 37 μW continuous wave laser (WITec focus innovations) with microscope objective numerical aperture NA=0.8 (Olympus 100x). The Raman was operated at the diffraction limit with a laser spot size of less than $1\mu\text{m}$.

Thermal sublimation of HZ-TIPS and OZ-TIPS deposition procedures. The precursor samples were immediately outgassed in the deposition chamber overnight prior to vacuum evaporation with typical base pressure close to 10^{-8} mbar. The perovskite substrate was held at room temperature during deposition. A commercial effusion Knudsen cell (Dr. Eberl MBE-Komponenten GmbH) equipped by quartz crucible was used; molecules were thoroughly degassed for several hours prior to the thermal sublimation procedure. The HZ-TIPS and OZ-TIPS precursors were thermally sublimated at temperatures of 257°C and 293°C , respectively.

XPS measurements. XPS measurements were performed in the Surface, Interface, and Nanostructure Science (SINS) beamline at the

Singapore Synchrotron Light Source (SSLS), equipped with a Scienta R4000 electron energy analyzer, facility with XPS instrument resolution of 0.05 eV. All photoemission spectra were collected at normal emission angle[32]. The samples discussed here were deposited in a separate preparation chamber and transferred ex-situ to the SINS beamline. Prior to the synchrotron measurements, all the samples were annealed to minimize adsorbed contaminants. All spectroscopic measurements were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of 1×10^{-10} mbar. The incident photon energy was calibrated using a sputter-cleaned gold foil in electrical contact with the sample. The energy spectra were referenced to the Au $4f_{7/2}$ core level peak at 84.0 eV.

UPS measurements. UPS measurements were performed using a VG ESCA Lab system, an ultrahigh vacuum (UHV) system with typical base pressure in the range of $\sim 10^{-10}$ mbar equipped with a He discharge lamp. The UV source was an unfiltered He I (21.2 eV) excitation and the sample was biased at -5V to extract the low-energy secondary cutoff. The UV light spot size on the sample is about 1 mm in diameter.

NEXAFS measurements. C K-edge NEXAFS experiments were carried out at the SINS beamline at SSLS. The C K-edge NEXAFS spectra were measured in total electron yield (TEY) mode by collecting the sample current with a photon energy resolution of 200 meV. The linear polarization factor of the X-ray beam was determined to be more than 90%. The beam line is equipped by a modified dragon-type monochromator with spherical gratings that allows the x rays impinge the sample at an angle of 90° . The intensity fluctuations originating from the synchrotron were corrected. Thus the obtained spectra were normalized to the photoelectron current on the refocusing mirror.

3 Results and discussion

3.1 Structural characterization

Prior to molecular deposition, several structural characterizations were carried out to assess the quality of the as-synthesized perovskite single crystal. The cubic single crystal of CsPbBr₃ composed of a Cs ion at the vertices of the cubic unit cell in which lead and halide ions form a PbX₆ octahedral at the center of the unit cell as presented in Fig 1c. To evaluate the degree of crystallinity, XRD diffraction patterns of CsPbBr₃ single crystals at room temperature were carried out as depicted in Fig 1d (the inset shows typical dimension of as-synthesized perovskites). Based on this result, the presence of four prominent reflection peaks in the range of 15°–60° is associated with most

relevant governing reflection that fits with the profile of the cubic perovskite phase.[33],[34] Sharp reflection peaks centered at 15°, 30°, 46° and 63° are correspond to <100>, <200>, <220>, and <400> direction, respectively. These values are in agreement with the earlier findings by Stoumpos and coworkers who proposed the orthorhombic perovskite structure[33]. AFM and SEM measurements were carried out to evaluate the topology of as-synthesized CsPbBr₃ single crystals. The SEM image in Fig. S1 and AFM image in Fig. 1e show that the perovskite surface displays a relatively smooth and flat morphological surface, with grain sizes of the order of 100 nm.

3.1 Optical properties of HZ-TIPS

The effect of HZ-TIPS molecules on CsPbBr₃ perovskite is investigated by monitoring any changes in its optical properties upon deposition. Fig. 2 shows a representative 3s HZ-TIPS molecular deposition sample measured with time-resolved PL spectroscopies. The effect of HZ-TIPS molecular doping on CsPbBr₃ Fig. 2a shows three emission peaks (424 nm, 446 nm, and 473 nm) that can be associated to the signature of HZ-TIPS. These additional peaks were not observed when we measured the bare perovskite sample (black curve).

To confirm these findings, we also performed similar experiment onto different substrate such as SiO₂ wafer (see Fig. S2 in SI). In addition, we verified in a separate experiment by depositing the molecule onto other substrate such as quartz (not shown). We found that the obtained emission peak positions are in agreement to the reported values here. Based on the earlier work of Li et al.[18], we noted that the emission PL peak of HZ-TIPS in chloroform solution was found at the higher wavelength region (704 nm) compare to the reported here.

Fig. 1 Chemical structure and characterization of Zethrenes on CsPbBr₃. (a) and (b) is the ball-stick model structure of HZ-TIPS and OZ-TIPS, respectively. (c) Representation of cubic structure CsPbBr₃. Each of respective colour balls indicates different atoms. (d) x-ray diffraction pattern of as-synthesized CsPbBr₃ single crystal. (e) Tapping mode AFM image taken prior to molecular deposition.

Figure 2 Optical properties of HZ-TIPS molecular doping on CsPbBr₃. (a) PL emission spectra of bare CsPbBr₃ (black solid line) versus doped (blue solid line). The latter curvature is multiplied by 10 for the sake of guidance for the eye. The inset indicates the enlargement of PL peak that correspond to the splitting of emission peak. (b) Time-resolved PL decay of bare CsPbBr₃ and its corresponding HZ-TIPS doped sample (c). A fitting curve is indicated by the solid red line.

We attribute the blue shifted emission peak arises in thermally-deposited HZ-TIPS sample to highly efficient charge transfer excited state processes that enhances better intramolecular π - π stacking interactions. Due to restriction of intramolecular molecular rotation, it allows one to suppress non-radiative pathways by means of intermolecular vibronic relaxation. This is evidently helpful in realizing efficient photoexcitation to occur in this system and leading to findings reported in Fig 2a. We also noted that the perovskite intrinsic emission peak (close to 522 nm) was blue-shifted with respect to the PL peak of perovskite without molecular doping (see raw data in Fig S3).

In addition, we also found that Raman spectra of CsPbBr₃ doped by HZ-TIPS displayed the characteristic feature of zethrene vibration mode in combination with the signal originates from the CsPbBr₃ (see supplementary information, Fig. S4).

To obtain further insights into PL quenching due to molecular doping, time-resolved PL (TRPL) spectra were recorded. The TRPL curve of pristine CsPbBr₃ (Fig. 2b) can be fitted with two exponential decays (see equation S1, SI). Here, we attribute emission lifetimes for fast and slow emission channels of τ_1 and τ_2 , respectively[35]. We may consider that the nonexponential decay curves in

HZ-TIPS doped case presented here as a manifestation of spatial and dipole orientation that affected due to nonuniformity of the local density of states driven by ensemble finite thickness of HZ-TIPS molecule on CsPbBr₃ surface. As a result, the average lifetime of 8.3 ns is determined (see equation S2 in SI). The extracted value is quite close to that of the previous reports[7, 8].

Further analysis of the HZ-TIPS doped samples exhibited a faster lifetime of about 3.6 ns (Fig. 2c). Furthermore, a 10-fold decrease of PL intensity of HZ-TIPS doped CsPbBr₃ is observed. This indicates that the non-radiative recombination processes were enhanced due to the introduction of HZ-TIPS deposition at such thin layer (estimated thickness is about 3 nm from AFM measurement, not shown).

Hence, we propose that the CsPbBr₃ surface is passivated by the HZ-TIPS molecular layer due to mediated non-radiative recombination and consequently this gives direct contribution to a significant PL emission peak reduction and a fast decay time. Such suppression on the radiative recombination process can be important for the development of photovoltaics as long as it could compensate the fast charge carriers of all inorganic perovskites.

3.2 Photoelectron measurements

We turn our attention to the interfacial formation of zethrene molecular doping on CsPbBr₃ single crystals. UPS and XPS experiments were carried out to investigate the electronic structures and possible chemical interactions at the HZ-TIPS/CsPbBr₃ interface. Any potential chemical peak shift in the corresponding XPS core level spectra will be a good indication whether band bending exists or not upon HZ-TIPS molecule deposition. Fig. 3(a-d) highlights the effect of HZ-TIPS molecular deposition monitored by the Pb4f, Br3d, C1s and Si2p XPS core levels. As expected, the intensities of Pb4f and Br3d peaks are progressively attenuated as shown in Fig. 3(a-b), while the increasing intensities of C1s and Si2p core levels with HZ-TIPS coverage are clearly visible in Fig. 3c and 3d, respectively.

To discuss further the effect of HZ-TIPS doping, we use pristine CsPbBr₃ core level peaks at the respective Pb4f and Br3d cases as a reference to monitor any changes upon HZ-TIPS molecular doping. The binding energy (BE) peaks that correspond to Pb4f_{5/2} and Pb4f_{7/2} core levels were found at 143.1 ± 0.02 eV and 138.3 ± 0.02 eV, respectively. The two peaks associated with the Br3d core levels are positioned at 69.10 ± 0.02 and 68.25 ± 0.02 eV, corresponding to the spin-orbit pair Br3d_{3/2} and Br3d_{5/2}, respectively.

These corresponding core level peak positions are in accordance to the earlier reports[26], which suggest that the under-study perovskite single crystal comprises of the expected contributing elements.

Figure 3 Comparison of photoemission spectra of HZ-TIPS and OZ-TIPS. XPS spectra of HZ-TIPS doped on CsPbBr₃ (a) Pb4f and (b) Br3d showed the attenuation signal of core level substrate. (c) and (d) represents the evolution of the C1s and Si2p of core-level spectra of HZ-TIPS molecule on CsPbBr₃. XPS spectra of OZ-TIPS doped on CsPbBr₃ (e) Pb4f, (f) Br3d, (g) C1s and (h) Si2p core levels. The respective core level spectra of bare perovskite (black), 1s zethrene-doped on perovskite (red), 3s zethrene-doped on perovskite (blue), 5s zethrene-doped on perovskite (pink).

Initially, 1 s HZ-TIPS and OZ-TIPS deposition shows small chemical shift in their respective core levels with respect to the bare substrate peaks. This might indicate that band bending takes place at such short deposition time. We infer that this event might occur due to the formation of island growth mode of zethrene molecule on the perovskite surface. Subsequent HZ-TIPS thicker layer was deposited onto the CsPbBr₃ surface, as a result, both Pb4f_{5/2} and Pb4f_{7/2} peaks are shifted to a higher BE position which give significant magnitude displacement close to 1.5 eV as shown in Fig. 3a. In a similar fashion, a red-shifted Br3d peaks were observed as illustrated in Fig. 3b. On the contrary, the OZ-TIPS deposition onto CsPbBr₃ surface led to a different result in which both core level of Pb4f and Br3d were shifted to lower BE value (0.6 eV) as shown in Fig. 3e and 3f. We also observed a similar trend from the Cs3d core levels of both experiments (Fig S5, SI). According to these findings, we propose that by choosing specific zethrene molecule with different electronic ground state may give control on the directionality of the charge transfer event at this particular organic/inorganic hybrid interface.

In the case of the C1s core level peak in HZ-TIPS-doped CsPbBr₃, we note that there is small chemical shift (0.2 eV) shown in Fig 3c. In the other hand, the subsequent molecular deposition trend in the OZ-TIPS case displays peaks that slightly shifted to a higher BE compare to the bare perovskite peak (0.4 eV) as shown in Fig 3g. We attributed this finding due to contribution of the additional number of carbon atoms (one benzene ring) in the OZ-TIPS compare to the HZ-TIPS. We note that there is an accompanying prominent peak close to 289 eV. This is a typical feature that could be attributed due to plasmon loss or unintentionally adventitious carbon.

In the other case, we found out that there are significant changes to the evolution of Si2p core level peaks. We determine that a comparable upshift of 1.5 eV that strongly pronounced in Si2p core level as

demonstrated in Fig. 3d. In addition, we also observed similar observation in the case of OZ-TIPS/CsPbBr₃ as shown in Fig. 3h. We propose that such large displacement in terms of Si2p core level peaks originates from the presence of the attached TIPS-substituent located at the bay region of zethrenes molecular backbone. These bulky groups possessing Si atoms at the bulky group could beneficially interact with the outmost layer of the CsPbBr₃ perovskite via dispersion force. Further explanation will be discussed in the following section.

In order to map the modified conduction and valence band levels as functions of molecular thickness, we have further investigated the energetics of the occupied states of perovskite using Ultraviolet Photoemission Spectroscopy (UPS). This method serves the work function (WF, ϕ) of the material which defined the required minimum kinetic energy (E_k) for photoelectrons to escape the organic thin film according to $E_k = h\nu - \phi - |EB|$, where $h\nu$ is the photon energy. The cutoff regions are indicated from the estimation of the energy onset from which the work function can be derived. In this study, we intentionally focus to thermally sublime at relatively thin layer of organic HZ-TIPS overlayer. This serves as an important precaution to minimize undesired artefacts that might be associated with photoelectron hole-screening effect in this system[36].

We note that the WF of pristine CsPbBr₃ single crystal is determined from the SECO experiment to be 3.7 eV. This value is consistent with the previous results which highlighted the good quality of the as-synthesized single crystal[5]. Subsequently, we deposited HZ-TIPS molecules for 1 s onto CsPbBr₃ surface that resulted an abrupt decrease of WF to 3.3 eV shown in Fig. 4a. Thus, as the molecular layer was continuously grown on top of CsPbBr₃ surface, the WF is gradually decreased and it retains a constant value close to 3.81 eV. According to these systematic

SECO measurements, the WF evolution was formed about 1.2 eV.

We also notice that the large interfacial dipole of beyond 2 eV was created at the interface when CsPbBr₃ surface was doped by OZ-TIPS molecules as demonstrated in Fig. 4c. There is an unusual long shallow tail at the thicker sample (7s deposition time) that could be originating from the mixed interplay of charging effect and disordered defects. Nevertheless, we believe that our experimental results here suggest a different outcome in comparison to previous studies of adsorbed molecule/perovskite interfaces[23, 26, 37]. In this work, we proposed that the interfacial electronic structure of all-inorganic CsPbBr₃ for a weakly-interacting adsorbate can be performed via surface charge transfer doping. Hence, the interfacial dipole formation across the HZ-TIPS/CsPbBr₃ heterojunction can be tailored by generally doped the perovskite surface with very few layers of zethrenes molecules.

The valence band edge spectra as a function of HZ-TIPS molecular deposition time are summarized in Fig. 4b. Based on the interpolation of the onset value of pristine CsPbBr₃ through the thickest HZ-TIPS layer, a small progression toward high BE was clearly observable with BE energy difference of ~0.32 eV. A noticeable behavior is also found in similar fashion for the case of OZ-TIPS/CsPbBr₃ as depicted in the Fig. 4d. In this systematic study, we found that at the initial molecular coverage (1s sample), the role of weak interfacial dispersion forces could be the governing factor at zethrene/CsPbBr₃ perovskite interface. Since the molecule-substrate interaction in this particular sample could be negligible compare to the intermolecular interaction, thus we relate our findings in the UPS data that the formation of such weak interfacial dipole at the initial stage of deposition could be initiated due to interplay contribution between the bond dipole and the weak electron redistribution[38, 39].

Figure 4 The evolution of UPS measurements of zethrene molecule on CsPbBr₃. (a) Low kinetic secondary cutoff (SECO) of HZ-TIPS as a function of molecular deposition time. (b) The close-up valence band structure of HZ-TIPS doped onto perovskites surface near to the zero binding energy. (c) SECO of OZ-TIPS as a function of molecular deposition time. (d) The close-up valence band structure of OZ-TIPS doped onto perovskites surface near to the zero binding energy. The E_F indicated by the dashed line here is correspond to the Fermi level of the substrate. The peak shifts are indicated by the dashed lines for the guides to the eye. The dashed dot arrows indicate the peak shifting according to the onset peak displacement upon the zethrene molecular doping on CsPbBr₃ surface.

In contrast, the dispersive interactions are competing with the molecule-substrate interactions that indirectly become decisive control at the thicker zethrene molecular layers. By taking into account the molecule-substrate and the intermolecular dispersion forces into the picture, we could tentatively propose that a collective transition of the randomized zethrene molecules occurs at the initial growth stage and it may led towards the dispersive

region at the thicker deposition case. This factor could increasingly play an important role at the thicker layers because the dominant commensurate molecular region is favorable to occurs. Therefore, further molecular alignment analysis is very useful to give more insight that will be illustrated in the following section using NEXAFS technique.

We further discuss the implication of the VL shift to the organic/inorganic interfaces due to several origins that have been previously reported in different reports.[40-42] The origin of such displacement could be governed by several reasons such as chemical bonding, permanent dipole orientation, image effect, interface states, surface rearrangement or charge transfer[40]. Since our system is mainly governed due to interaction of physisorbed zethrene on the perovskite, then we could tentatively rule out four aforementioned plausible contributions. Based on the obtained UPS and XPS data, we found that there is an indication of a band bending behavior related with the charge transfer event at the interface. The surface rearrangement that might occurs in the perovskite needs to be clarified with further detail using theoretical calculations that beyond the scope of the current work.

3.3 NEXAFS measurements

To determine the molecular orientation of HZ-TIPS on CsPbBr₃, we performed near edge x-ray absorption fine structure (NEXAFS) spectroscopy across the carbon K-edge with different angles of incidence. We first oriented the incoming photon beam at low grazing incident angle (20°) with respect to the sample surface to obtain angular dependent NEXAFS spectra. In this case the photon polarization (*E*) is mostly out-of-plane with respect to the sample surface. Fig. 5a-c show carbon *K*-edge NEXAFS spectra at different photon incidence angles of HZ-TIPS thin film as a function of molecular thicknesses with 1s, 3s and 5s deposition

times, respectively. The experimental NEXAFS geometry and the molecular conformation are schematically depicted in Fig. 5d. To acquire the angle-dependent measurements, we vary the incoming photon beam from 30°, 60°, to normal incidence (90°).

The NEXAFS spectra at different molecular coverages exhibit distinct peak enhancements due to contribution from the respective transition molecular resonance states. It is well recognized that the resonant intensity is strongly influenced by the directionality of the *E* vector. Thus, the enhancement of intensity can be determined when *E* is parallel to the molecular orbital vector. On the contrary, the absorption intensity could be suppressed when *E* is perpendicular to the molecular orbital vector[43, 44]. In this analysis, we assign the resonance peaks in accordance to the two resonance regimes (π^* and σ^* electronic transitions) that are commonly found in the 283-290 eV energy range.

The origin of the resonance peak in the NEXAFS spectrum below 285 eV and 287 eV corresponds to the π^* resonances form due to the electronic transitions from the initial states into the unoccupied π^* molecular orbitals (LUMOs), whereas the 292 eV and 296 eV feature are attributed to the σ^* resonance transition into LUMOs[45]. We tabulated the output respective resonance peaks extracted from NEXAFS measurements in Table 1.

Table 1. Resonance transition peaks of HZ-TIPS molecules with different deposition times. The uncertainty in binding energy values is ± 0.05 eV.

Sample	π_1^* (eV)	π_2^* (eV)	σ_1^* (eV)	σ_2^* (eV)
1s HZ-TIPS on CsPbBr ₃	284.6	287.8	292.5	296.7
3s HZ-TIPS on CsPbBr ₃	284.4	287.7	292.5	296.9
5s HZ-TIPS on CsPbBr ₃	284.1	287.6	292.3	96.7

Two NEXAFS spectra in Fig. 5b and 5c shows the presence of angular dependence profile compared to the result in Fig. 5a. To emphasize the results, we plotted the respective enlargement at the photon energies 286–290 eV as shown in Fig. 5e and 5f. The latter exhibited peculiar demonstration of the angular dependence of HZ-TIPS on CsPbBr₃ surface.

Figure 5 Carbon K-edge NEXAFS spectra of HZ-TIPS on CsPbBr₃ in different molecular thicknesses. (a) 1s deposition time. (b) 3s deposition time. (c) 5s deposition time. (d) An illustration of HZ-TIPS molecular conformation where alpha is the average tilt angle. (e) and (f) is the enlargement of NEXAFS spectra centered at 286–290 eV which clearly shows the angular dependence behaviour taken from 3s and 5s sample, respectively.

The angular dependent π^* resonance intensity at different incidence angles can be formulated as follows[46]:

$$I \propto A \cdot \left\{ \frac{P}{3} \left[1 + \frac{1}{2} (3 \cos^2 \theta - 1) (3 \cos^2 \alpha - 1) \right] + \frac{(1-P)}{2} \sin^2 \alpha \right\}$$

Where A is a constant, $P = 0.90$ is associated to the linear polarization factor[47, 48], α is the average tilt angle of molecular backbone normal to the substrate surface. Thus, linear plots of I versus $\cos^2 \theta$ were used to extract the slope and intercept, used to determine the unknown parameter, the average tilt angle (α). From this analysis, we determined the average tilt angles to be $47.4^\circ \pm 0.2^\circ$ and $57.9^\circ \pm 0.3^\circ$ for 3 s and 5 s deposition time, respectively (further detail can be found in the Supporting information). For the 1 s sample, we cannot deduce the molecular orientation since the data acquisition at 60° could not be achieved due to technical issue arises during experiment. Based on this angular dependence approach, the molecular orientation of HZ-TIPS is most likely lifted with respect to the perovskite surface. This could be rationalized due to role of bulky TIPS-substituent that introduces steric hindrance toward molecular arrangement on the perovskites surface.

2 Conclusions

In summary, we investigated the molecular doping of zethrene molecules with two different natures of electronic properties, namely, open-shell and closed-shell ground electronic state on CsPbBr₃ perovskite single crystal using combined synchrotron-based spectroscopic techniques. The directionality of band bending behaviour of the respective case can be determined from the photoemission measurements. The downward band bending occurs in the case of HZ-TIPS/CsPbBr₃ interface. In contrast, an upward band bending was observed in the case of OZ-TIPS/CsPbBr₃ interface. We attributed these findings due to distinctive electronic ground states between HZ-TIPS and OZ-TIPS. In addition, the average tilt angle determination using NEXAFS technique reveals the anisotropic dependence in the π^* symmetry transition of the carbon K-edge

(284–288 eV range) for few layer-thick of zethrene molecules. Our result shows a tunable interfacial alignment of low band gap zethrene molecules on all-inorganic perovskite surfaces that could play an important role in tuning the electronic properties of hybrid organic-inorganic heterostructure devices.

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