## Supporting Information

## Molecular Functionalization of All-Inorganic Perovskite CsPbBr<sub>3</sub> Thin Films

Arramel<sup>a,\*</sup>, Hu Pan<sup>b</sup>, Aozhen Xie<sup>c,d,e</sup>, Xinmao Yin<sup>a,f</sup>, Chi Sin Tang<sup>a,f,g</sup>, Kei Ikeda<sup>h</sup>, Muhammad Haris Mahyuddin<sup>i,j</sup>, Muhammad Fauzi Sahdan<sup>a</sup>, Dingguan Wang<sup>a,b</sup>, Kazunari Yoshizawa<sup>h</sup>, Hong Wang<sup>c,d</sup>, Muhammad Danang Birowosuto<sup>c,\*</sup>, Cuong Dang<sup>c,d,e</sup>, Andrivo Rusydi<sup>a,f,g,k</sup>, Andrew Thye Shen Wee<sup>a,1</sup> and Jishan Wu<sup>b,\*</sup>

<sup>a</sup>Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117551, Singapore.

<sup>b</sup>Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore.

°CINTRA UMI CNRS/NTU/THALES, Singapore 637553, Singapore.

<sup>d</sup>School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore.

Energy Research Institute @NTU (ERI@N), Nanyang Technological University, Singapore 637553, Singapore.

<sup>f</sup>Singapore Synchrotron Light Source (SSLS), National University of Singapore, 5 Research Link, Singapore 117603, Singapore.

<sup>g</sup>NUS Graduate School for Integrative Sciences and Engineering, National University of Singapore,

Singapore 117456, Singapore.

<sup>h</sup>Institute for Materials Chemistry and Engineering and IRCCS, Kyushu University, 744 Motooka Nishiku, Fukuoka 819-0395, Japan.

<sup>i</sup>Research Group of Advanced Functional Materials, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia.

<sup>j</sup>Research Center for Nanoscience and Nanotechnology, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia

<sup>k</sup>NUSNNI-NanoCore, National University of Singapore, Singapore 117411, Singapore.

<sup>1</sup>Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore,

6 Science Drive 2, Singapore 117546, Singapore.

\*Email: phyarr@nus.edu.sg; mbirowosuto@ntu.edu.sg; chmwuj@nus.edu.sg



**Fig. S1** Structure property and surface inspection of as-deposited CsPbBr<sub>3</sub> thin films on 300-nm thick  $SiO_2$  wafer. (a) X-ray diffraction pattern taken from  $10^\circ-60^\circ 2\theta$  range. Inset shows the corresponding primitive unit cell. (b) AFM tapping mode shows a representative cubic-shaped CsPbBr<sub>3</sub> at low perovskite coverage. The scale bar 400 nm. (c) The cross sectional of grey line shown in Fig. b indicating that the nominal thickness of CsPbBr<sub>3</sub> films used in this study is typically about 38 nm.



**Fig. S2** X-ray photoemission spectra of the thermally-sublimated heptazethrene on CsPbBr<sub>3</sub> with different molecular thicknesses. The first, second and third columns are associated to the core level of C1s, O1s, and Si2p (except in HZ-F, where F1s is presented instead). The respective spectra correspond to 0 Å (black), 2.20 Å (red), 6.60 Å (blue), 11Å (pink), 13.2 Å (green), 16.5 Å (dark blue) and 33 Å (magenta).

## Additional chemical state discussion.

Irrespective of the doped perovskites, the general trend of C1s intensities are increasing as a function of molecular coverage as illustrated in Fig. S2(a-c). In contrast, the XPS intensities of the O1s core level (Fig. S2 d-f) originates from the silicon wafer signal is suppressed as the molecular thickness gradually developed from few-layers up to multilayer-thick regime. In the case of HZ-M deposition (Fig. S2e), the occurrence O1s signal originates from the mesityl-substitutent containing oxygen atoms within its functional groups.

To substantiate our finding, as the HZ-TIPS or HZ-F coverage increases, the intensities of contributing element such as Si2p or F1s core levels centered at respective  $104.55 \pm 0.02$  eV and  $687.2 \pm 0.02$  eV are well pronounced in Fig. S2g and S2i. On the contrary, the Si2p signal of HZ-M (Fig. S2h) doping case where no silicon element residing in the zethrene backbone was attenuated due to the fact that photo-emitted electron were hardly escape from the underlying silicon wafer as the nominal thickness of HZ-M molecular layer goes thicker. The evolution of C-F bonding in the C1s core level of HZ-F molecular doping (Fig. S2c, light-blue arrow) around 288.8  $\pm$  0.02 eV and we also present the C1s line shape deconvolution analysis from pristine CsPbBr<sub>3</sub> upon HZ-F deposition as shown in Figure S3.

S-5



**Fig. S3** Deconvoluted XPS spectra of HZ-F on CsPbBr<sub>3</sub>. (a) C1s core level of pristine CsPbBr<sub>3</sub> (0 Å), the observed peak is correspond to the adventitious carbon peak. (b) C1s core level peak of 2.20 Å-thick HZ-F molecules on perovskite. (c) C1s core level peak of 6.60 Å-thick HZ-F molecules on perovskite. (d) C1s core level peak of 11 Å-thick HZ-F molecules on perovskite. (e) C1s core level peak of 33 Å-thick HZ-F molecules on perovskite. (f) Integrated peak plot acquired from the respective C-C peak centered at 285.5 eV and C-F centered at 288.8 eV.

**The average tilt angle and error tilt angle analysis**. Rearrangement of the formula (1) in the main text to obtain the following equation:

$$I = \left[\frac{AP}{2}(3\cos^{2}\alpha - 1)\right]\cos^{2}\Theta + \left[\frac{A(1-P)}{2}\sin^{2}\alpha + \frac{AP}{2}(1-\cos^{2}\alpha)\right]$$
(S1)

where

$$m = \frac{AP}{2} (3\cos^2 \alpha - 1)$$
 is corresponds to the gradient  
$$c = \frac{A(1-P)}{2} \sin^2 \alpha + \frac{AP}{2} (1 - \cos^2 \alpha)$$
 is corresponds to the "y-intercept"

From the equation of the gradient, *m*:

$$\cos^{2} \alpha = \frac{1}{3} \left( \frac{2m}{AP} + 1 \right)$$
(S2)
$$\sin^{2} \alpha = \frac{2}{3} \left( 1 - \frac{m}{AP} \right)$$
(S3)

Substituting (S6) into the equation for the y-intercept, *c*, we get:

$$A = 3c + \frac{m}{P} \tag{S4}$$

The following values of the gradient, m and y-intercept, c, and their corresponding errors are taken from the linear fitting values computed in the origin software. For example, we present the average tilt angle determination for thin layer of HZ-M molecule on CsPbBr<sub>3</sub> as follows:



Fig. S4 A representative of linear fit plot  $\pi^*$  versus  $\cos^2\theta$  of HZ-M molecules with 2.20 Å-thickness on

CsPbBr<sub>3</sub>.

From the above plot, we can extract:

- a)  $m = -0.04 \pm 0.007$
- b)  $c = 1.19 \pm 0.004$

Thus, from Equation (S3), the relative error in A is:

$$\left|\frac{\Delta A}{A}\right| = \left|\frac{\Delta c}{c}\right| + \left|\frac{\Delta m}{m}\right| \tag{S5}$$

c)  $A = 3.52 \pm 0.01$ 

From Equation (S5), let  $y = cos\alpha$ , the relative error in y is as follows:

$$\frac{\Delta y}{y} = \frac{1}{2} \left( \left| \frac{\Delta m}{m} \right| + \left| \frac{\Delta A}{A} \right| \right)$$
(S6)

d) The value of the tilt angle using Equation (S6) was found to be 54.94°.

From (S6), the absolute error, 
$$\Delta y = 0.05$$
  
With  $\Delta y = \cos (\alpha + \Delta \alpha) - \cos (\alpha)$ , (S7)

Using Taylor series we expanded equation S7:

$$\Delta y = \cos \left( \alpha \right) - \Delta \alpha \sin \left( \alpha \right) - \cos \left( \alpha \right) = -\Delta \alpha \sin \left( \alpha \right) \tag{S8}$$

Thus, 
$$\Delta \alpha = \left| \frac{\Delta y}{\sin(\alpha)} \right|$$
 (S9)

With  $\Delta y = 0.05$  and  $\alpha = 56.5^{\circ}$ , and resulted  $\Delta \alpha = 0.23^{\circ}$ .



Fig. S5 Normalized PL intensity of HZ-F on ITO as a function of molecular layer thicknesses. The

inset depicted the respective nominal thickness value.



**Fig. S6** Comparative TR-PL decay profile of HZ-F molecules on CsPbBr<sub>3</sub> thin films. The black (red) correspond to the direct measurement (after 1 week) of molecular adlayer deposition onto the perovskite surface.



Fig. S7 Time-resolved PL decay curve of pristine CsPbBr<sub>3</sub> thin films. Raw data (black) and fitted curve

(red) are shown. The charge carrier components are indicated with their corresponding weight factor.



**Fig. S8** Representative PL spectra of HZ-M–molecularly doped on CsPbBr<sub>3</sub>. (a) Black line indicated PL spectrum of deposition of 2.20 Å HZ-M on Au substrate, whereas the orange line indicated PL spectrum of 2.20 Å-thick HZ-M deposition onto CsPbBr<sub>3</sub>/Au. (b) TR-PL decay profile 2.20 Å-thick HZ-M molecules on Au with  $425 \pm 25$  nm emission wavelength. (c) TR-PL decay profile 2.20 Å-thick HZ-M molecules on CsPbBr<sub>3</sub>/Au with  $425 \pm 25$  nm emission wavelength (d) TR-PL decay of 2.20 Å-thick HZ-M molecules on CsPbBr<sub>3</sub>/Au with  $425 \pm 25$  nm emission wavelength (d) TR-PL decay of 2.20 Å-thick HZ-M molecular deposition onto CsPbBr<sub>3</sub>/Au with  $525 \pm 25$  nm emission wavelength. The excitation source is 10 MHz pulsed laser at 355 nm excitation wavelength. White lines represent the fitting curve of the respective cases.



Fig. S9 Optimized geometric structures obtained from DFT calculations for (a, d) HZ-TIPS, (b, e) HZ-

M, and (c, f) HZ-F on CsPbBr<sub>3</sub>(110) with the end of (top) methyl group and (bottom) benzene ring. Color legend for atoms: Cs (cyan), Pb (blue), Br (brown), Si (orange), C (gray), H (white), F (purple), O (red).