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Unexpected surface interactions between fluorocarbons and hybrid organic inorganic perovskites evidenced by PM-IRRAS and their application towards tuning the surface potential

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Supporting information

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1. General information

All reactions were carried out under an argon atmosphere. Solvents were dried over activated alumina columns on a MBRAUN Solvent Purification System (SPS-800) unless otherwise noted. All reagent-grade chemicals were obtained from commercial suppliers and were used as received unless otherwise stated. Anhydrous dimethylformamide (DMF) was purchased from chemical suppliers (Aldrich or Acros Organics) and used as received. FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100 using a KBr pellet. Analytical thin layer chromatography was performed using silica gel 60 F254 pre-coated plates (Merck) with visualization by ultraviolet light or potassium permanganate. Flash chromatography was performed on silica gel (0.043-0.063 mm).

The surface potential was measured in ambient condition by Kelvin probe technique using vibrating gold grid reference electrode (Kelvin probe S, Bescoke Delta Phi, diameter 2.5 mm). The DC bias is controlled by a feedback circuit (Kelvin control S, Bescoke Delta Phi).

2. Synthesis

Porphyrins **P1**[1] and **P2**[2] were prepared and purified according to published procedures.
Metallation of **P2** was achieved as indicated below.

Zn-**P2**. **P2** (10 mg) was placed in a 10 mL round bottom flask and dissolved in 5 mL of DCM. A 5-fold excess of $(CH_3CO_2)_2Zn\cdot 2H_2O$ (9.3 mg) was dissolved in 1.0 ml of MeOH, added to the porphyrin solution, and further stirred for 16 h. The solvents were evaporated under reduced pressure and the dark solid was taken up in dichloromethane (DCM) and purified by column (eluent: DCM / MeOH 98:2). The purple band was collected and the solvents were removed under reduced pressure to yield Zn-**P2** as a bright purple solid (11 mg, 100%). IR (cm^{-1}): 506, 718, 744, 933, 1110, 1220, 1342, 1552, 2926.

Co-**P2**. **P2** (15 mg) was placed in a 25 mL round bottom flask and dissolved in 15 mL of DMF. $(CH_3CO_2)_2Co\cdot4H_2O$ (30 mg) was added and the solution was heated at reflux under argon for 40 min. until no further change by UV-vis. The solution was cooled to room temperature and diluted with water (50 mL). The dark precipitate was filtered, washed with water until the wash solution was clear, and air-dried. The precipitate was then taken up in DCM and purified on an aluminum oxide column eluting with DCM. The product was collected and the solvent removed under reduced pressure to afford Co-**P2** as a pink solid (7 mg, 55%). IR (cm^{-1}): 715, 740, 935, 1104, 1227, 1338, 2923.

Pb-**P2**. **P2** (10 mg) was placed in a 5 mL round bottom flask and dissolved in 2.5 mL of DMF. $(CH_3CO_2)_2Pb\cdot3H_2O$ (39 mg) was added and the solution was heated at reflux under argon for 4 h until no further change by UV-vis. The solution was cooled to room temperature and diluted with water (25 mL). The dark precipitate was filtered, washed with water until the wash solution was clear, and air-dried. The precipitate was collected by dissolving in MeOH, filtering, and removing the solvent under reduced pressure to afford Pb-**P2** as a green solid (5 mg, 40 %). IR (cm^{-1}): 742, 821, 928, 1111, 1223, 1340, 2926.

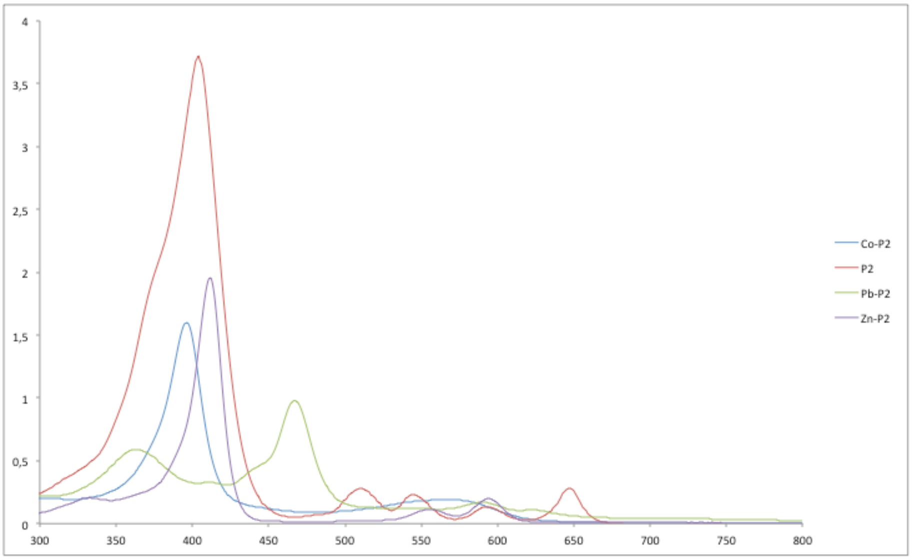


Fig. S1 Uv-Vis electronic absorption spectra of **P2**, Zn-**P2**, Co-**P2**, Pb-**P2** in DCM.

3. Crystal structure of Zn-P2

Crystallographic data was acquired at CESAMO (UMR 5255) on a Bruker APEX 2 DUO. A single crystal of Zn-**P2**, obtained from slow evaporation of an ethanol solution, was mounted and immersed in a stream of nitrogen gas [*T* = 150(2) K]. Data were collected, using a microfocus sealed tube of Mo Kα radiation (*k* = 0.71073 Å) on a KappaCCD diffractometer. Data collection and cell refinement were performed using APEX2 2013.10-0 (Bruker AXS Inc.), and SAINT v8.34A (Bruker AXS Inc.). Data reduction was performed using SAINT v8.34A (Bruker AXS Inc.). Correction for absorption was performed using multi-scan integration as included in SADABS V2012/1 (Bruker AXS). Structure solutions were found by charge flipping methods (SUPERFLIP (Palatinus & Chapuis, 2007) EDMA (Palatinus et al., 2012)) and refined with (SHELXL)

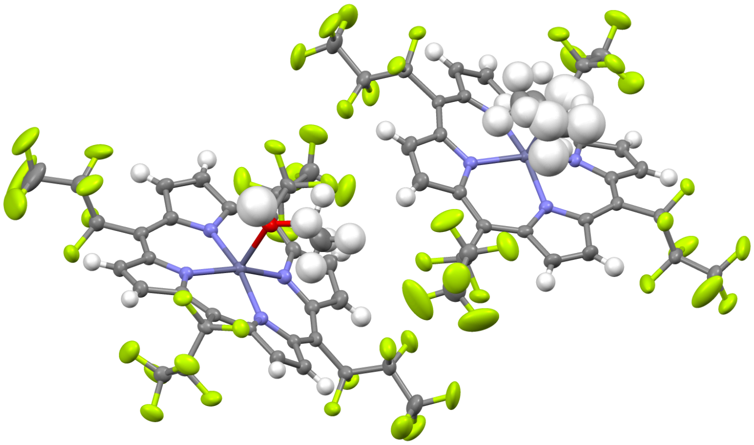


Fig S2 Solid-state structure of Zn-**P2** (ccdc 1866532)

Table S1. Crystal data and structure refinement for Zn-**P2**.

Identification code	1866532
Empirical formula	C68 H28 F56 N8 O2 Zn2
Formula weight	2183.72
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic,P -1
Unit cell dimensionsa =	13.9830(9) A alpha = 77.1460(10) deg.
	b = 16.9424(11) Abeta = 74.2360(10) deg.
	c = 19.1273(11) A gamma = 75.997(2) deg.
	Volume4171.3(5) A^3
	Z, Calculated density 2,1.739 Mg/m^3
Absorption coefficient	0.749 mm^-1
	F(000)2144
Crystal size	0.850 x 0.800 x 0.300 mm
Theta range for data collection	1.538 to 27.844 deg.
Limiting indices	-18<=h<=18, -22<=k<=22, -23<=l<=25
Reflections collected / unique	59692 / 19661 [R(int) = 0.0312]
Completeness to theta =	25.24299.5 %
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission	0.7456 and 0.6605
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	19661 / 11 / 1264
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0429, wR2 = 0.1208
R indices (all data)	R1 = 0.0553, wR2 = 0.1271
Extinction coefficient	n/a
Largest diff. peak and hole	1.236 and -0.810 e.A^-3

4. Fabrication of $CH_3NH_3PbI_3$ perovskite films

The ITO substrates (1.5 x 1.5 cm, ITO thickness 150 nm, Visiontek) were cleaned by sonicating in water, acetone, ethanol and isopropanol solution for 10 min each. Then, the substrates were cleaned under UV-ozone for 15 min after air drying. Immediately after ozone cleaning, the **PEDOT:PSS** solution was spin-coated on the clean substrate at 3000 rpm for 60 s and dried in an oven at 110 °C for 60 min. After that, the **PEDOT:PSS** coated ITO substrates were transferred to a nitrogen-filled glove box to spin coat the perovskite solution.

The perovskite solution was prepared by dissolving 0.3857 g methylammoniumiodide (Dyesol) and 0.4857 g of lead acetate (99.9 % Sigma Aldrich) in 1.25 mL of DMF and stirred for 30 min inside the glovebox. 120 μL of this solution was spin-coated onto the **PEDOT:PSS** coated ITO substrate at 2500 rpm for 120 s and annealed for 25 min at 100 °C. For better crystallization, the substrates were pre-heated at 100 °C for 10 min prior to spin coating of perovskite solution.

Adlayer deposition

To deposit adlayers, 150 μL of neat **PFDT** or **PFO** solution was drop casted on perovskite film and incubated for 15 min followed by rinsing copiously with trifluorotoluene (TFT). For deposition of **P1** and **P2**, the same method was followed using 1 mM solution of **P1** and **P2** in TFT and toluene respectively. For **P2** the rinsing was done with toluene.

5. X-ray diffraction on HOIP

The XRD pattern was acquired using a Bruker D8 Advanced Davinci Powder X-Ray Diffractometer with a Cu- K_α ($\lambda = 1.5406$ Å) source.

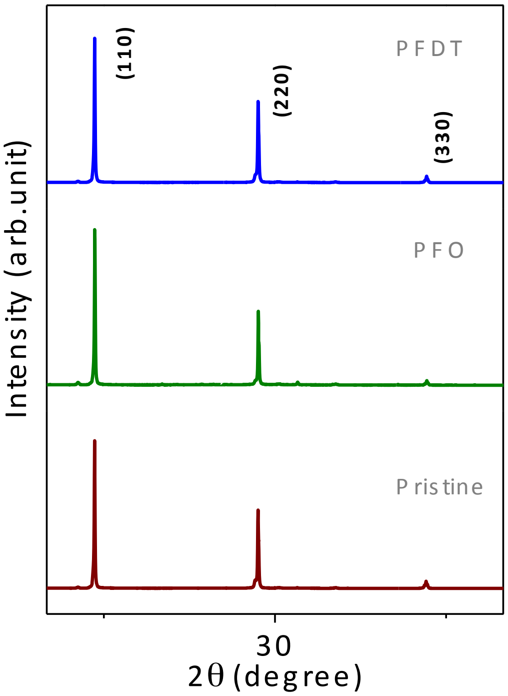


Fig. S3 XRD pattern of pristine, **PFO** and **PFDT** modified perovskite surface.

6. X-ray photoemission spectroscopy

High-resolution photoemission spectra were recorded using a XPS apparatus (SPECS Surface Nano Analysis GmbH). A photon beam with the energy of 1486.7 eV was generated from an aluminum anode in a microfocus X-ray (XR-MF) source. The XR-MF source was also equipped with a quartz crystal mirror as a monochromator, producing the monochromatic Al Kα X-ray beam. A PHOIBOS 150 Hemispherical Energy Analyzer (HEA) with a nine-single-channel electron multiplier detector (MCD-9) was used to collect photoemission spectra. High-resolution spectra were recorded with a pass energy of 20 eV, which gave a full-width at half maximum (FWHM) of ~0.5 eV for the Au $4f_{7/2}$ peak. We calibrated the binding energy of the photoemission spectra with reference to C 1s at 285.3 eV.

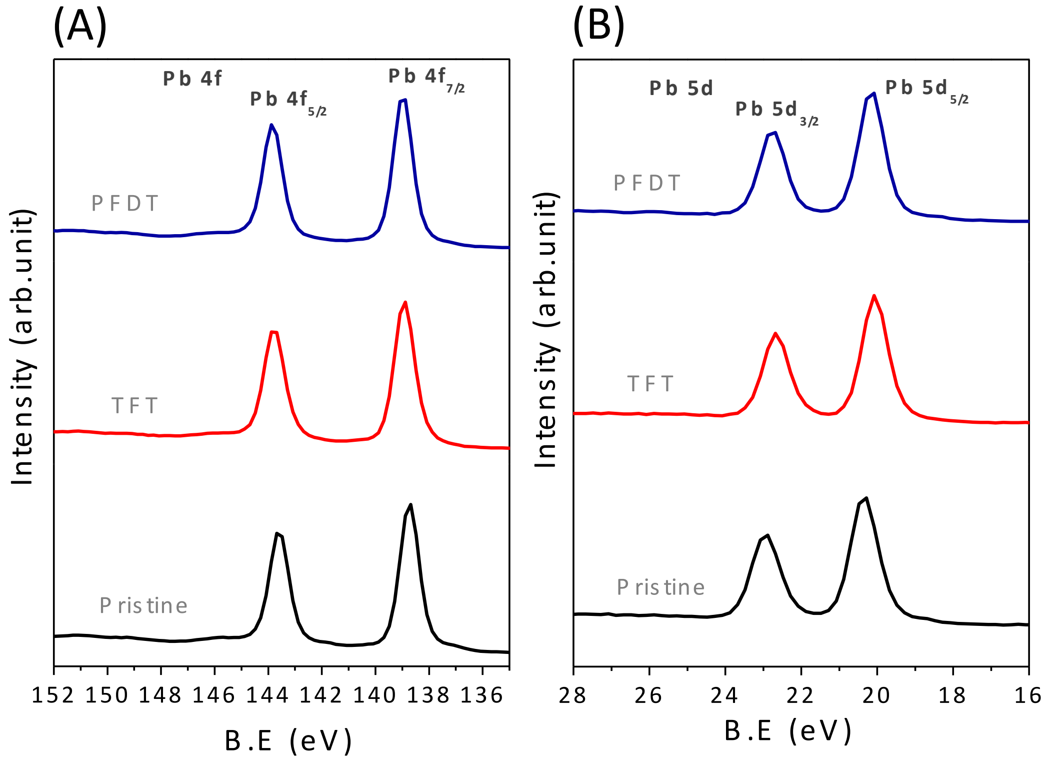


Fig. S4 XPS spectra of (A) Pb 4f and (B) Pb 5d from pristine perovskite, TFT and **PFDT** passivated perovskite surface.

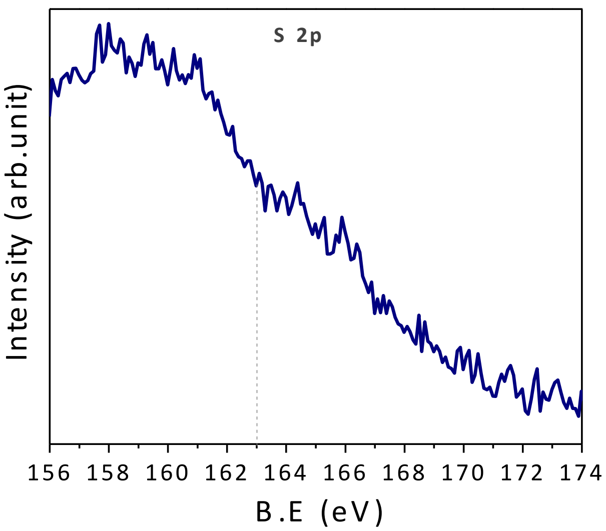


Fig. S5 XPS spectra of S 2p of **PFDT** passivated perovskite surface.

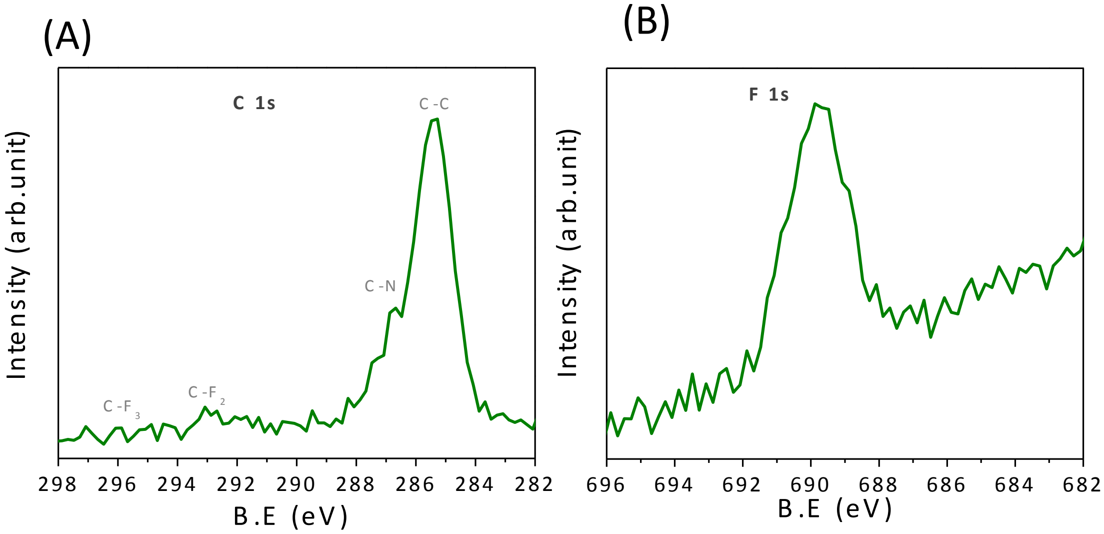


Fig. S6 (A) C1s and (B) F1s XPS spectra of **PFO** passivated perovskite surface.

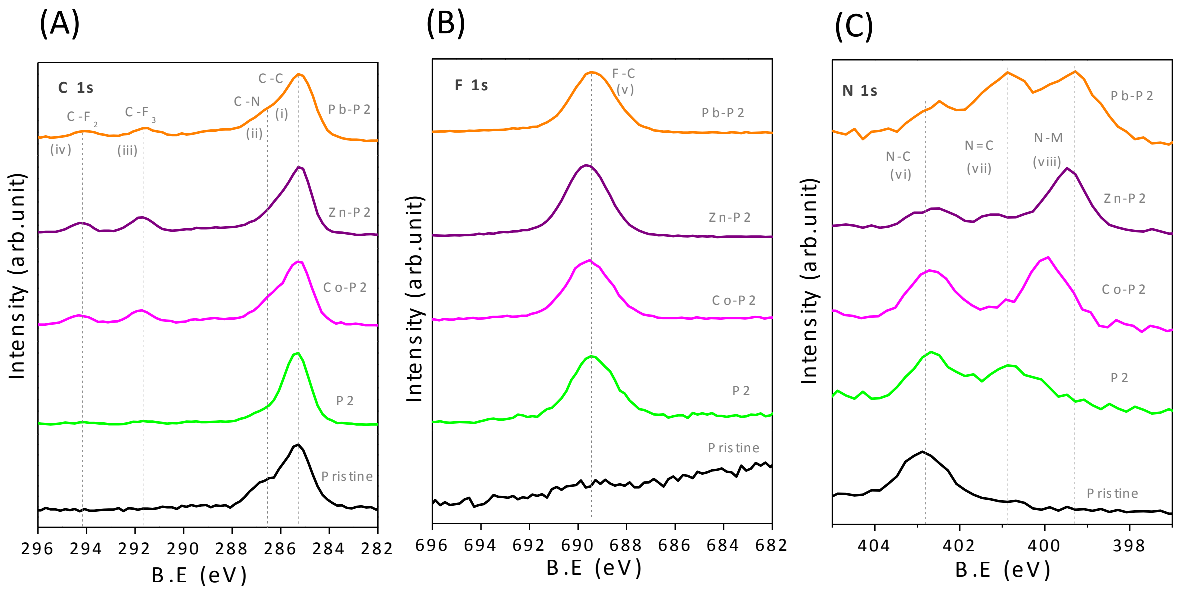


Fig. S7 Fig. S7 XPS spectra of (A) C 1s (B) F 1s and (C) N 1s from pristine perovskite, **P2** and different metal based **P2** modified perovskite surface.

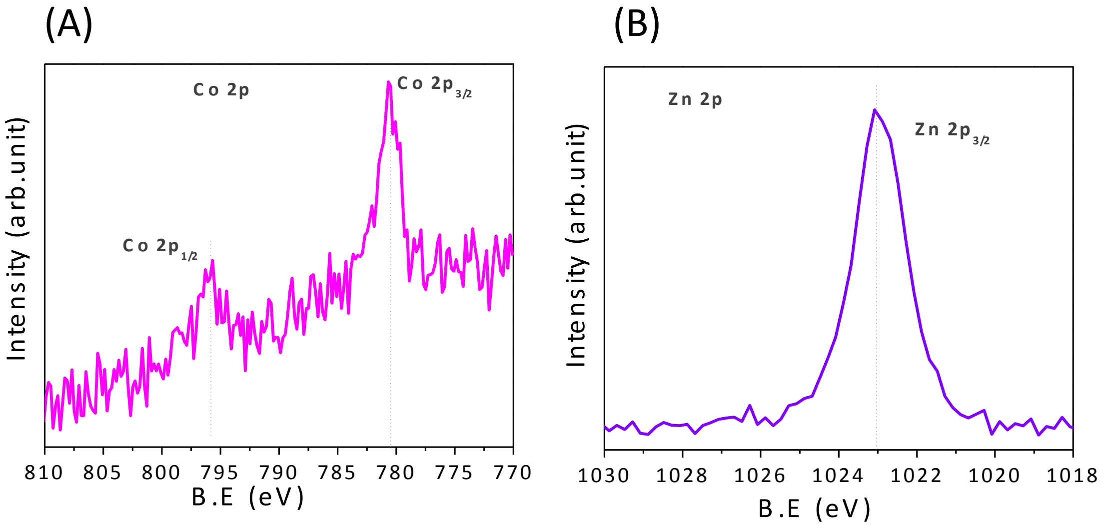


Fig. S8 XPS spectra of (A) Co 2p and (B) Zn 2p from Co and Zn metal based **P2** modified perovskite surface.

7. Infrared spectroscopy

PM-IRRAS experiments

PM-IRRAS spectra of **PFDT**, **PFO** and **P1** on perovskite and gold substrates were recorded on a ThermoNicolet Nexus 670 FTIR spectrometer at a resolution of 4 cm^{-1}, by coadding eight blocks of 1500 scans (4 h total acquisition time). All spectra were collected in a dry-air atmosphere. Experiments were performed at an incidence angle of 75° using an external homemade goniometer reflection attachment.[3] The infrared parallel beam (modulated in intensity at frequency ω_i lower than 5 KHz) was directed out of the spectrometer with an optional flipper mirror and made slightly convergent with a first BaF_2 lens (191 mm focal length). The IR beam passed through a BaF_2 wire grid polarizer (Specac) to select the p-polarized radiation and a ZnSe photoelastic modulator (PEM, Hinds Instruments, type II/ZS50). The PEM modulated the polarization of the beam at a high fixed frequency, ω_m=100 KHz, between the parallel and perpendicular linear states. After reflection on the sample, the double modulated (in intensity and in polarization) infrared beam was focused with a second ZnSe lens (38.1 mm focal length) onto a photovoltaic MCT detector (Kolmar Technologies, Model KV104) cooled at 77 K. The polarization modulated signal I_{AC} was separated from the low frequency signal I_{DC} (ω_i between 500 and 5000 Hz) with a 40 KHz high pass filter and then demodulated with a lock-in amplifier (Stanford Model SR 830). The output time constant was set to 1 ms. The two interferograms were high-pass and low-pass filtered (Stanford Model SR 650) and simultaneously sampled in the dual channel electronics of the spectrometer. In all experiments, the PEM was adjusted for a maximum efficiency at 2500 cm^{-1} to cover the mid-IR range in only one spectrum.

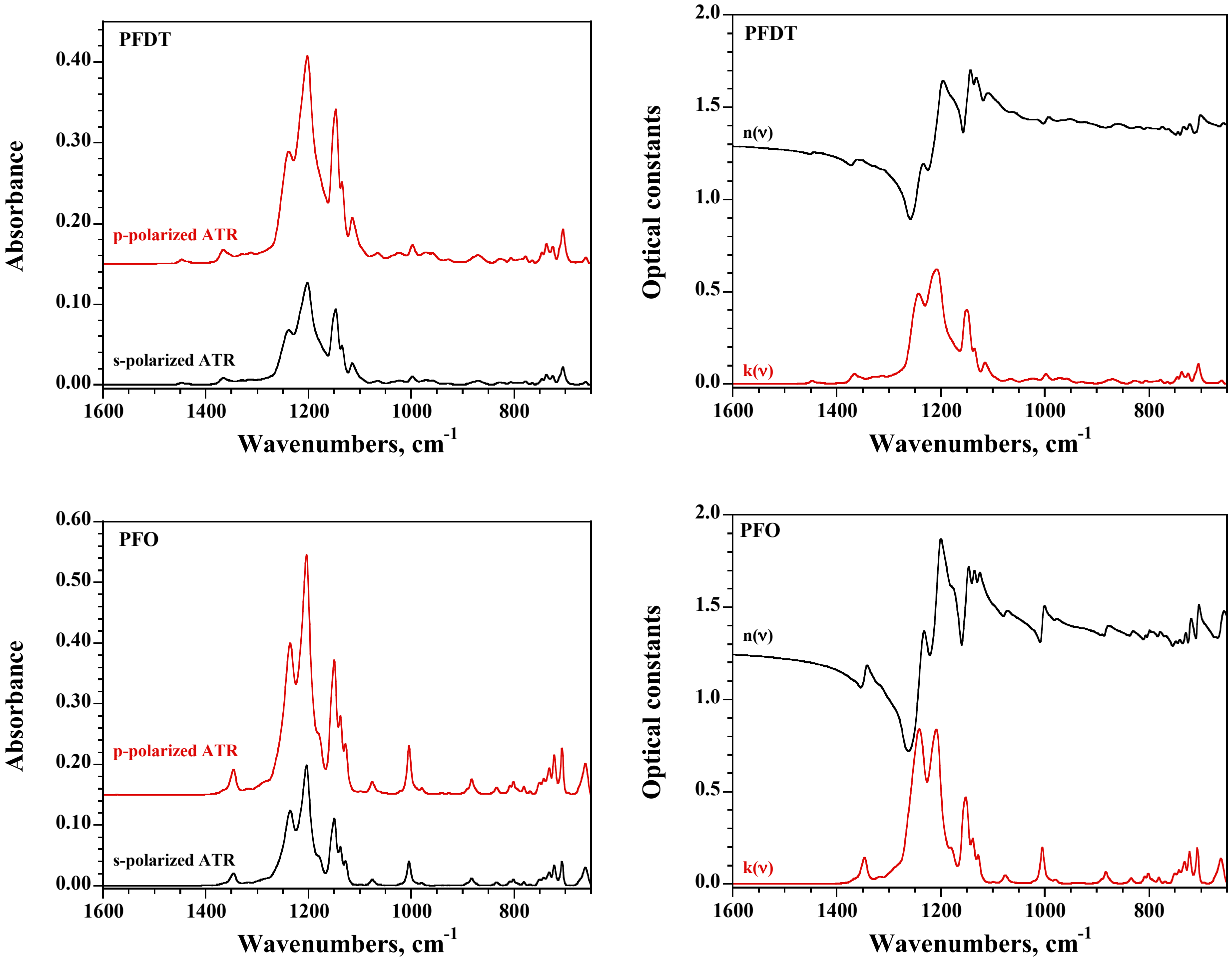
For calibration measurements, a second linear polarizer (oriented parallel or perpendicular to the first preceding the PEM) was inserted between the sample and the second ZnSe lens. This procedure was used to calibrate and convert the PM-IRRAS signal in terms of the IRRAS signal (i.e., $1-\frac{R_p(d)}{R_p(0)}$ where $R_p(d)$ and $R_p(0)$ stand for the p-polarized reflectance of the film/substrate and bare substrate systems, respectively).[4,5]

ATR experiments, determination of the optical constants and spectral simulation of the IRRAS spectrum for a compact monolayer

The ATR spectra of **PFDT**, **PFO** and **P1** compounds were recorded with a ThermoNicolet Nexus 670 FTIR spectrometer equipped with a liquid nitrogen cooled narrow-band mercury cadmium telluride (MCT) detector using a Silver-Gate (germanium crystal) ATR accessory (Specac). The electric field of the infrared beam was polarized either perpendicular (s-polarized) or parallel (p-polarized) to the plane of incidence with a BaF_2 wire grid polarizer (Specac). Each spectrum was obtained, at a resolution of 4 cm^{-1}, by coadding 500 scans (**P1**), 200 scans (**PFDT**) and 32 scans (**PFO**).

The isotropic optical constants (refractive index $n(\bar{v})$ and extinction coefficient $k(\bar{v})$) of **PFDT**, **PFO** and **P1** compounds have been determined from polarized ATR spectra, using the procedure decribed by Dignam et al.[6] For each compounds, we have checked that the intensities of the bands in the p-polarized ATR spectrum are the double than those measured in the s-polarized ATR spectrum, that is expected for an isotropic layer. The refractive indices in the visible were set to 1.30 for **PFO**, 1.33 for **PFDT** and 1.40 for **P1**.

The computer program used to calculate the IRRAS spectra for a compact monolayer of **PFDT**, **PFO** and **P1** compounds deposited onto perovskite/Au substrate is based on the Abeles' matrix formalism,[7,8] which has been generalized for anisotropic layers.[9] Several parameters must be fixed in the program such as the the thickness of the monolayer, the refractive index (set to 2.5) and the thickness (set to 80 nm) of the perovskite film, the angle of incidence (set to 75°) and the polarization of the infrared beam. The p-polarized reflectance of the covered $R_p(d)$ and bare $R_p(0)$ substrates have been calculated using the spectral dependence of the optical constants of **PFDT**, **PFO**, **P1** and of gold.[10]



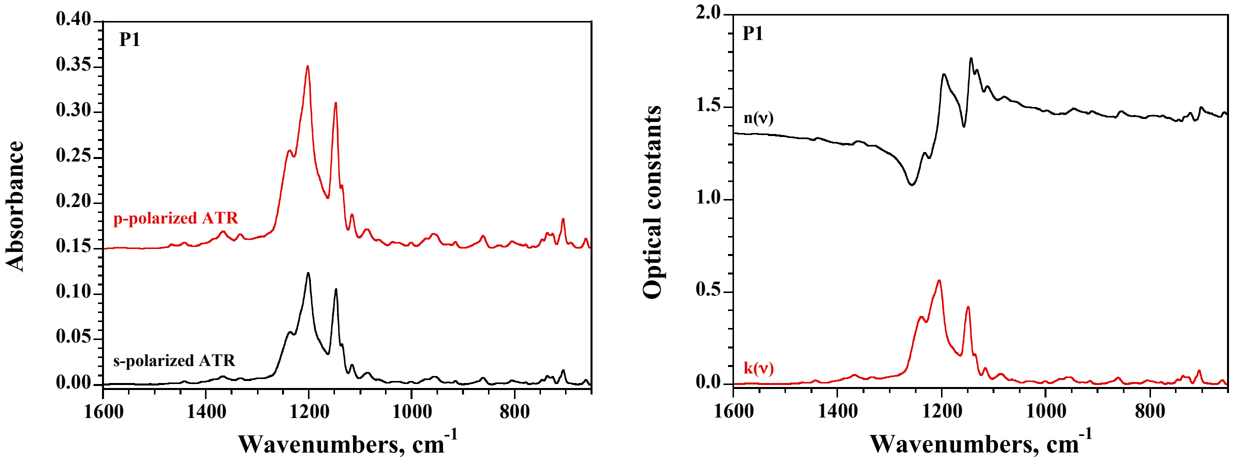


Fig. S9 *P*- and *s*-polarized ATR spectra and Isotropic optical constants of **PFDT**, **PFO**, and **P1**.

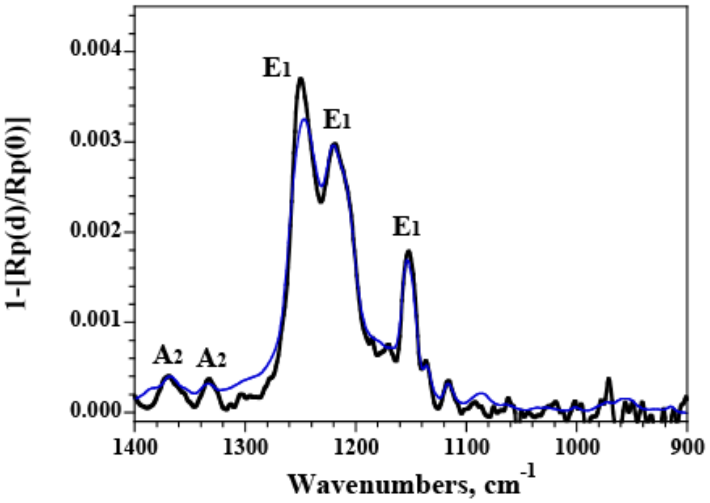


Fig. S10 PM-IRRAS spectrum of **P1** modified perovskite surface (black line). The simulated spectrum (blue line) shows the thickness of the film to be 8Å.

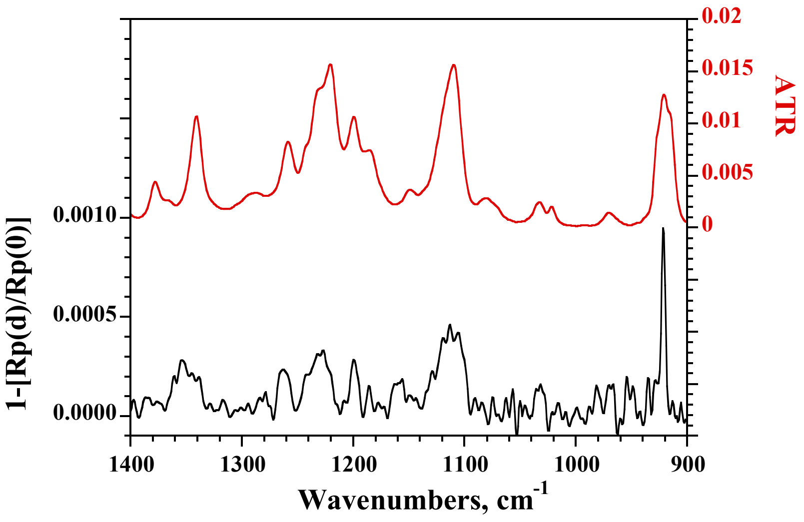


Fig. S11 ATR spectrum of **P2** (red line) and PM-IRRAS spectrum of **P2** modified perovskite surface (black line).

Table S2 Peak position and corresponding vibrational modes of $CH_3NH_3PbI_3$ perovskite.

Position (cm^{-1})	Peak assignment
1577	Asymmetric NH_3^+ bend
1469	Symmetric NH_3^+ bend
1423	Asymmetric CH_3 bend
1385	Symmetric CH_3 bend
1250	CH_3-NH_3^+ rock
955	C-N stretch
911	CH_3-NH_3^+ rock

8. Scanning electron microscopy

SEM images were acquired using a JEOL 7800 scanning electron microscope.

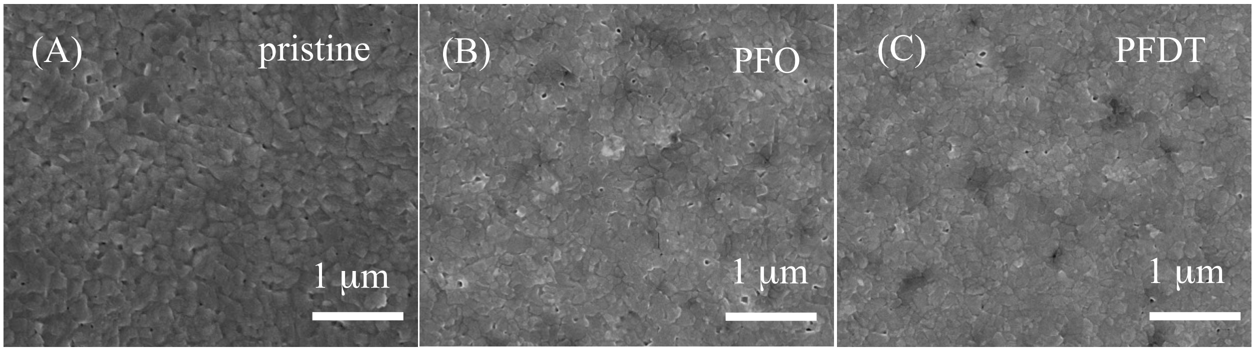


Fig. S12 SEM images of (A) only pristine, (B) **PFO** and (C) **PFDT** modified perovskite surface.

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