Controlling and modulating terahertz signals is of fundamental importance to allow systems level applications. We demonstrate an innovative approach for controlling the propagation properties of terahertz (THz) radiation, through use of both the excitation optical wavelength (colour) and intensity. We accomplish this using two-dimensional (2D) layered hybrid trihalide perovskites that are deposited onto silicon substrates. The absorption properties of these materials in the visible range can be tuned by changing the number of inorganic atomic layers between the organic cation layers. Optical absorption in 2D perovskites occurs over a broad spectral range above the bandgap, resulting in free carrier generation, as well as over a narrow spectral range near the bandedge due to exciton formation. We find that only the latter contribution gives rise to photo-induced THz absorption. By patterning multiple 2D perovskites with different optical absorption properties onto a single device, we demonstrate both colour selective modulation and focusing of THz radiation. These findings open new directions for creating active THz devices.
**Results**

**Perovskite synthesis and film growth.** The perovskites precursors were synthesized by mixing PbI$_2$, CH$_3$NH$_3$I and C$_6$H$_5$C$_2$H$_4$NH$_3$I in a dimethylformamide solution with a typical concentration of 0.5 M. The amounts of precursors were kept at corresponding stoichiometric ratios to form (C$_6$H$_5$C$_2$H$_4$NH$_3$)$_2$(CH$_3$NH$_3$)$_{n-1}$(PbI)$_n$ where $n = 1$, 2, and 3. Figure 1a shows the typical chemical structure of $n = 1$, 2, and 3 perovskites, where two adjacent layers of octahedral [PbI$_4$]$^{2-}$ are sandwiched between [C$_6$H$_5$C$_2$H$_4$NH$_3$]$^+$ and [CH$_3$NH$_3$]$^+$, and its Ruddlesden–Popper (R–P) mixtures with CH$_3$NH$_3$PbI$_3$, to enable colour selective THz modulation using plasmonic structures fabricated on a semiconductor substrate. In the R–P phase, the alternate layers of organic cations and inorganic anion arrange to form an intercalated system of insulating and conducting layers, creating a superlattice structure. By chemically changing the number of the inorganic layers between the adjacent organic layers, the absorption band can be tuned over a wide region of the visible spectral range. When deposited on select semiconductor substrates, we observe enhanced broadband THz absorption, as compared to the bare semiconductor. However, this only occurs when the incident radiation corresponds to the wavelength range associated with exciton absorption.

**Photoluminescence and THz transmission measurements.** We initially measured the transmitted broadband THz radiation through different samples, while optically exciting the perovskite side of the sample with filtered radiation from a halogen lamp (360–800 nm). In Fig. 1b, we show the optically induced THz transmission spectra measured using ($n = 2$) 2D perovskites deposited directly onto a high resistivity silicon wafer. Care was taken in these measurements to minimize thermal heating artifacts. The THz throughput is seen to decrease approximately uniformly from 0.1 to 1.6 THz with increasing lamp flux. In
transfer at the interface. This may yield insight into the enhanced graphene/semiconductor bilayer structures have been shown to absorption upon optical illumination. It is worth noting that and perovskite that dramatically enhances broadband THz (Supplementary Note 2). It is the interface between the silicon ovskite layer itself does not contribute to the THz absorption absorption, demonstrating that carrier generation in the per- dielectric layer (200 nm), there is no appreciable increase in THz However, when the perovskite layer is placed on a thicker n the perovskite/silicon samples exhibited nearly the same behavior as = fi = 1 and = 1 to 1.8 t = 3, that exhibit various bandgaps between 2.5 eV for = 1 to 1.8 eV for = 3 [31]. In Fig. 2a, we show the absorption and photoluminescence emission spectra for each =-variant. These PL spectra show a slight red-shift compared with the absorption bandedges. This occurs because the photoexcitations preferentially relax to the impurities of larger =-number (although they are only of a trace amount). This agrees also with published data [31, 52], demonstrating both the quality and distinctness of each material. To better understand the excitation wavelength dependence on the THz absorption in the 2D perovskites/Si samples, we optically illuminated each sample using a series of 50 nm wide bandpass filters ranging from 450 to 800 nm. A

Fig. 2 Excitation spectra of the THz extinction based on various 2D perovskites. a Photoluminescence spectra of the 2D perovskites used in this work and the associated UV-vis absorption (black curves). b Schematic depicting the measurement concept. The 2D perovskite samples were photoexcited using a filtered halogen lamp. c Transmission spectra of the silicon/perovskite samples for = 1 layer (green), = 2 layer (yellow), and = 3 layer (red) 2D perovskites. The strong absorption of THz radiation occurs in the same narrow-band optical range as the photoluminescence spectra in a. d An expanded view of the device showing multiple 2D perovskites layers forming a superlattice. The schematic shows two possible mechanisms for exciton dissociation into free carriers. Mechanism A: excitons that are normally confined to the lead-halide plane, exhibit overlapping wavefunctions in the superlattice and tunnel into the silicon substrate, where they can dissociate thereby contributing to the THz absorption. Mechanism B: excitons diffuse through edge states (grain boundaries) where they dissociate into free carriers [38]. These free carriers could diffuse to the underlying silicon through the voids in the polycrystalline films
schematic diagram of the experimental setup is shown in Fig. 2b, with the corresponding data shown in Fig. 2c.

Interestingly, THz absorption in these samples increases appreciably only when the wavelength of the incident optical radiation corresponds to the wavelength of the exciton resonance, but not at higher energies that corresponds to band-to-band transition. To understand this phenomenon, we consider the sample structure. When a thin perovskite film is deposited onto a substrate, it consists of a stack of 2D R–P layers, each of which naturally forms a quantum well. As shown schematically in Fig. 2d, the resulting structure forms a superlattice, in which the barriers are thin, such that the exciton wavefunctions in adjacent wells strongly overlap. Upon illumination with above bandgap optical excitation, both free carriers and excitons are photogenerated in each layer. In the case of isolated layers, the photoexcitations are usually confined to their respective lead-halide planes. However, in a superlattice structure the photoexcitations may be delocalized, which allows for tunneling between layers. The optically induced THz absorption data shown in Fig. 2c suggests that only excitons can tunnel vertically through the superlattice and into the silicon substrate. There, they can dissociate and add to the overall carrier density in the Si substrate (Supplementary Fig. 2), thereby substantially increasing the THz absorption. Free carriers, on the other hand, do not appear to be able to tunnel through the multiplayers and into the silicon substrate. Thus, only excitation wavelengths causing exciton formation lead to increased THz absorption. This also explains why we do not observe any THz absorption when a 2D perovskite film is deposited onto a dielectric (Supplementary Fig. 2). Blancon and co-workers recently showed that excitons in 2D perovskites can diffuse to lower energy edge states where they can dissociate into free carriers. This may be an alternate explanation for increased carrier generation in the silicon substrate, where excitons are able to reach the substrate via voids between grain boundaries. Finally, we note that excitons do not dominate the absorption in 3D MAPbI₃ perovskites and, thus, we do not observe an analogous wavelength (colour) selective control of the THz absorption. Instead, 3D perovskites behave much the same as conventional semiconductors for this specific application, as discussed in Supplementary Notes 3 and 4.

Active THz devices. This discovery can be used to create optical wavelength (colour) selective THz modulators. Figure 3 summarizes the basic idea and experimental results. We fabricated a series of periodic subwavelength aperture arrays in 200 nm thick aluminum thin films deposited on high resistivity silicon wafers. Subsequently, a n = 1, n = 2, or n = 3 hybrid perovskite thin film was deposited on top of the Al structure, so that it was in direct contact with the silicon only inside of each aperture, as shown schematically in Fig. 3a. Figure 3b shows that the n = 1 sample exhibits no optical intensity dependence when illuminated at 700 nm (Fig. 2c), since that wavelength does not correspond to photogenerated excitons in the perovskite layer. The transmission spectra are also measured as a function of the optical intensity and shown in Fig. 3c (n = 1 perovskite) through Fig. 3e (n = 3 perovskite), when illuminated using narrow-band radiation at the optimal wavelengths determined in Fig. 2. In each case, with increasing optical intensity, the increased THz absorption within the apertures leads to lower overall THz transmission. These data further demonstrate that the observations are associated with increased exciton photogeneration rather than due to local heating or other artifacts.

A significant advantage of perovskites over other conventional crystalline semiconductors is that thin films can be fabricated
using comparatively simple solution-based and vapor-phase deposition techniques. Thus, multiple perovskites can be deposited on different regions of the same device. To demonstrate the efficacy of this approach, we fabricated another plasmonic structure in which three separate subwavelength aperture arrays with different periodicities, though with identical aperture radius to aperture spacing ratios, were placed adjacent to one another, as shown schematically in Fig. 4. We designed the number of apertures in each section to ensure that the magnitude of the measured THz amplitude for the lowest order resonance was approximately identical, regardless of frequency. We then deposited 2D perovskite thin films with different $n$ values on top of each region. The basic fabrication steps, shown in Fig. 4, utilized a series of poly-dimethyl siloxane (PDMS) shadow masks to define the deposition regions. The resulting array sections had lowest order resonance peaks at $\sim 0.22$ THz ($n = 3$), $\sim 0.41$ THz ($n = 2$), and $\sim 0.95$ THz ($n = 1$).

Figure 5 summarizes the experimental results that demonstrate the utility of colour selective modulation of THz radiation. The transmission spectrum associated with the device is shown in Fig. 5a and consists of three bands of resonances, one for each aperture array region. Each of these bands consists of multiple resonances that can be related directly to the periodicity and dielectric properties of the adjacent materials (perovskites and silicon). In contrast to the earlier demonstrations discussed above, we now use long pass optical filters to progressively reduce and ultimately erase multiple bands of resonances. Using the experimental geometry shown in Fig. 2b with a 700 nm long pass filter, the resonances in the lowest frequency band of resonances (near 0.2 THz) can be reduced in amplitude (Supplementary

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**Fig. 4** Schematic showing solution-based fabrication of colour selective THz modulator. (clockwise) The solution processed 2D perovskites having different $n$, are spin coated selectively onto the different sections of the aperture array-based structure using a series of PDMS masks

**Fig. 5** Excitation selective THz modulator. 

(a) Schematic of a resonant device that consists of three different aperture array sections coated with different 2D perovskite layers as denoted. 

(b) The THz spectrum of the device in the dark showing the resonant response for all three sections. The lowest order resonances for each section have peaks at 0.22 THz, 0.41 THz, and 0.95 THz, respectively, that correspond directly to the aperture spacing in each section. The smaller bands next to the primary bands correspond to higher order plasmonic resonances.

(c) (left to right) THz spectra of the device illuminated with 700 nm long pass filter, 600 nm long pass filter, and 500 nm long pass filter, respectively. The optical excitation range is shown above each spectrum. For example, a 600 nm long pass filter allows for illumination from 600 to 850 nm. Thus, a broader optical spectrum can span multiple exciton excitation ranges. The entire device was uniformly illuminated in each case.
Note 5) in a controlled manner by varying the lamp flux. For the maximum optical intensity used here, this band of resonances disappear completely (Fig. 5b). However, the higher frequency resonances remain unchanged, because only the region covered by the \( n = 3 \) perovskite is affected. When a 600 nm long pass filter is used, only the resonance bands near 0.2 and 0.4 THz, corresponding to the \( n = 3 \) and \( n = 2 \) perovskites undergo modulation (Fig. 5c). Finally, when a 500 nm long pass filter is used (Fig. 5d), all three sets of resonances are impacted.

The perovskite/Si structure opens numerous possibilities for other device implementations. As an example, we demonstrate the ability to optical control the focusing of THz radiation. The specific implementation relies on creating a circular aperture in which the diameter can be altered in a colour selective manner. For a circular aperture, the intensity variation along the axis is determined by the incident wavelength, aperture size, and distance from the aperture, and can be described analytically by Rayleigh-Sommerfeld diffraction. We patterned a silicon substrate with cylindrical concentric rings \( n = 1, 2, \) and \( 3 \) perovskites, as shown schematically in Fig. 6a. Using the same illumination sequence as in Fig. 5 with a 100 GHz narrow-band frequency THz source, we were able to change the effective aperture radius from 11 mm (700 nm long pass), to 8 mm (600 nm long pass) to 4 mm (500 nm long pass). In Fig. 6b, we show the numerically simulated THz spatial pattern for the three apertures mentioned above, along with cross-sections in the designated planes using both experimental THz imaging measurements and numerical simulations. The measured and simulated cross-sections agree well and correspond to focal lengths of 10 mm (11 mm radius aperture), 25 mm (8 mm radius aperture), and 40 mm (4 mm radius aperture), as shown in Fig. 6c.

**Discussion**

In summary, we have demonstrated that 2D hybrid organic–inorganic lead-trihalide perovskites offer a number of unique characteristics for fabricating active THz devices that distinguish them from structures fabricated using conventional semiconductors. Notably, the bandgaps of these materials, as well as the associated exciton absorption band, can be easily altered. Moreover, these perovskites can be deposited using a variety of conventional thin film deposition techniques and they yield a photoresponse that is dramatically larger than the bare semiconductor onto which they are deposited. Using a plasmonic structure over which multiple perovskites are deposited, we have shown near complete suppression of transmission resonances using only relatively low intensity narrow-band excitation from a halogen lamp. Thus, this approach overcomes the limitations encountered with existing modulators: the devices require only relatively simple fabrication techniques and when compared...
to optically induced modulation, THz absorption now depends upon the excitation optical wavelength and a halogen lamp can be used instead of an ultrafast laser source. These materials offer new possibilities for greater control over active THz devices.

**Methods**  

**Fluorescence and UV-visible measurements.** Fluorescence spectra were taken with an optical fiber based spectrometer (Ocean Optics USB4000ES) by exciting the films on glass substrates with a 447 nm semiconductor laser (50 mW). A 500 nm long pass filter was used before the spectrometer to block the residual laser beam. UV-visible absorption spectra were carried out with Agilent Cary UV-vis Spectrophotometer (200 nm to 2.5 μm).

**FTIR measurements.** Photo-induced free carrier absorption was characterized using an FTIR (Fourier transform infrared) spectrometer in various samples. A 2.8 eV (442 nm) cw diode laser was used as the optical pump and the IR probe beam was provided by the FTIR. The 2D perovskite films were deposited on Si and KBr substrates and placed in a cryostat in which the temperature could be varied from 45 to 300 K. The pump and probe beams were co-incident on the sample films, and the transmission, T, and change of the transmitted probe beam (ΔT) was detected by a DLaTGS detector. The photoabsorption spectrum was calculated from measurements of the fractional change in transmission (ΔT/T) using approximately 6000 scans of the FTIR spectrometer with the pump beam on and off.

**Multi-perovskite device fabrication.** The patterned multi-perovskite structures were prepared using a step-by-step spin-coating method. A silicon wafer with thin substrates and placed in a cryostat in which the temperature could be varied from 4.2 to 300 K. The pump and probe beams were co-incident on the sample films, and the transmission, T, and change of the transmitted probe beam (ΔT) was detected by a DLaTGS detector. The photoabsorption spectrum was calculated from measurements of the fractional change in transmission (ΔT/T) using approximately 6000 scans of the FTIR spectrometer with the pump beam on and off.

**THz transmission and imaging measurements.** The transmission spectra were obtained using standard THz time-domain spectroscopy (THz TDS) measurements. We used nonlinear optical crystals for both THz generation and detection stimulated by an ultrafast Ti:sapphire laser. The broadband, linearly polarized THz radiation generated by the emitter was collected and collimated by an off-axis parabolic, such that the radiation was normally incident on the samples. A second off-axis parabolic mirror placed after the filter was used to focus the transmitted THz radiation onto the detection crystal for measurement via electro-optic sampling. For THz imaging, we used a narrow-band polarized electro-optic source operating at 0.1 THz. The transmitted radiation was imaged using a THz focal plane array.

**Data availability.** The data that support the findings of this study are available from the corresponding authors upon reasonable requests.

**References**

1. Tomouchi, M. Cutting-edge terahertz technology. Nat. Photon. 1, 97–105 (2007).
2. Rahm, M., Li, J.-S. & Padilla, W. J. THz wave modulators: a brief review on different modulation techniques. J. Infrared Millim. Terahertz Waves 34, 1–27 (2013).
3. Tao, H. & Reconfigurable terahertz metamaterials. Phys. Rev. Lett. 103, 147401 (2009).
4. Zhu, W. M. et al. Microelectromechanical Maltese-cross metamaterial with tunable terahertz anisotropy. Nat. Commun. 3, 1274 (2012).
5. Pitchappa, P. et al. Micro-electro-mechanically tunable metamaterial with enhanced electro-optic performance. Appl. Phys. Lett. 104, 151104 (2014).
6. Ushu, M. et al. Switchable scattering meta-surfaces for broadband terahertz modulation. Sci. Rep. 4, 5708 (2014).
7. Kleine-Ostmann, T., Dawson, P., Pierz, K., Hein, G. & Koch, M. Room-temperature operation of an electrically driven terahertz modulator. Appl. Phys. Lett. 84, 3555–3557 (2004).
8. Chen, H.-T. et al. Active terahertz metamaterial devices. Nature 444, 597–600 (2006).
9. Chen, H.-T. et al. A metamaterial solid-state terahertz phase modulator. Nat. Photon. 3, 148–151 (2009).
10. Ju, L. et al. Graphene plasmonics for tunable terahertz metamaterials. Nat. Nanotechnol. 6, 630–634 (2011).
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