

ARTICLE

DOI: 10.1038/s42005-018-0082-8 OPEN

Extremely reduced dielectric confinement in twodimensional hybrid perovskites with large polar organics

Bin Cheng¹, Ting-You Li¹, Partha Maity², Pai-Chun Wei¹, Dennis Nordlund³, Kang-Ting Ho¹, Der-Hsien Lien⁴, Chun-Ho Lin¹, Ru-Ze Liang¹, Xiaohe Miao⁵, Idris A. Ajia², Jun Yin², Dimosthenis Sokaras³, Ali Javey⁴, Iman S. Roqan², Omar F. Mohammed² & Jr-Hau He¹

Two dimensional inorganic-organic hybrid perovskites (2D perovskites) suffer from not only quantum confinement, but also dielectric confinement, hindering their application perspective in devices involving the conversion of an optical input into current. In this report, we theoretically predict that an extremely low exciton binding energy can be achieved in 2D perovskites by using high dielectric-constant organic components. We demonstrate that in (HOCH₂CH₂NH₃)₂Pbl₄, whose organic material has a high dielectric constant of 37, the dielectric confinement is largely reduced, and the exciton binding energy is 20-times smaller than that in conventional 2D perovskites. As a result, the photo-induced excitons can be thermally dissociated efficiently at room temperature, as clearly indicated from femtosecond transient absorption measurements. In addition, the mobility is largely improved due to the strong screening effect on charge impurities. Such low dielectric-confined 2D perovskites show excellent carrier extraction efficiency, and outstanding humidity resistance compared to conventional 2D perovskites.

¹ Computer, Electrical, and Mathematical Sciences and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia. ² KAUST Solar Center, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia. ³ Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA. ⁴ Electrical Engineering and Computer Sciences, University of California, Berkeley, CA 94720, USA. ⁵ Core Laboratories, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia. These authors contributed equally: Bin Cheng, Ting-You Li. Correspondence and requests for materials should be addressed to J.-H.H. (email: jrhau.he@kaust.edu.sa)

Use to high absorption coefficient, intense photoluminescence (PL), low electron-hole recombination rate and long carrier diffusion length, organic-inorganic hybrid perovskites (3D perovskites) are regarded as one of the leading candidates of next-generation photovoltaics¹⁻⁴. Recently, two-dimensional layered organic-inorganic halide perovskites (2D perovskites) have attracted attention as an alternative to 3D perovskites in photovoltaic devices because of their improved stability and moisture resistance⁵⁻¹⁰. In addition, as a result of weak Van der Waals force between the organic layers, 2D perovskite nanosheets can be produced by solution-based method^{8,9,11} and mechanical exfoliation¹², making them a new platform for low-dimensional nano-electronics/optoelectronics.

However, following the general trend of quantum confinement¹³, the exciton-binding energy of 2D perovskites is much larger compared to their 3D counterpart. Moreover, since the conventional organic linkers used in 2D perovskites, such as $C_6H_5(CH_2)_2NH_3^+$ and $C_4H_9NH_3^+$, have small dielectric constants, dielectric confinement also emerges and makes the exciton-binding energy even larger¹³⁻¹⁶. Such large excitonbinding energy makes it difficult for excitons to form free carriers via thermal activation. Accordingly, the strong combined effect of quantum and dielectric confinement makes the carrier mobility in 2D perovskites approximately two orders of magnitude lower than that in 3D perovskites¹⁷.

In order to fully utilize the optoelectronic properties of 2D perovskites for photoelectric applications, intrinsic methods to lower the confinement in 2D perovskites are urgently required. Quantum confinement can be reduced by increasing the width of the inorganic semiconductor layer in 2D perovskites (see Supplementary Note 1), but even when the width of the inorganic layer is enlarged by five times, the binding energy is still up to 200 meV¹⁸. Therefore, it is necessary to develop an alternative approach to "weaken" the dielectric confinement in 2D perovskites. However, the current method of reducing dielectric confinement by intercalation can only lower the exciton-binding energy by tens of meV¹⁹, which is not enough for achieving effective thermal dissociation of excitons at room temperature.

In this report, we hypothesize that dielectric confinement in 2D perovskites can be largely reduced by using a high-dielectric constant organic component. Specifically, we demonstrate that $(HOCH_2CH_2NH_3)_2PbI_4$ (2D_EA perovskites)²⁰, in which the dielectric constant of the organic component is as high as 37.7²¹, has a 20-times smaller exciton- binding energy and dozens of times larger carrier mobility compared to high-dielectric confinement 2D perovskites. Our results indicate that by reducing the dielectric confinement by using an organic component with a large dielectric constant, the carrier separation efficiency is largely improved. Finally, we find that low-dielectric-confined 2D perovskites are highly stable under humidity, due to the strong hydrogen bonding between the organic layers.

Result

Crystal preparation and optical characterization. We adopted the image charge model to gain insight into the relationship between the exciton-binding energy and dielectric constant of organic components in 2D perovskites¹³. We focused on two organic groups, ethanolamine (EA, HOCH₂CH₂NH₃⁺) (Fig. 1a) and phenethylamine (PEA, $C_6H_5(CH_2)_2NH_3^+$) (Fig. 1b), because their dielectric constants are quite different. According to our simulation (see Supplementary Note 2), when the dielectric constant is ~3.3¹⁴, the Bohr radius describing the mean distance between the electron and hole in the exciton will decrease and accordingly the exciton-binding energy will be

largely enhanced (Fig. 1c), indicating a strong dielectric confinement. Conversely, as the dielectric constant of the organic layers increases, the dielectric screening effect will be enhanced, so that the Coulomb force between electron and hole of the exciton will decrease, leading to an increased Bohr radius and decreased exciton-binding energy. If the dielectric constant of the organic layer is sufficiently large, we can even achieve an excitonbinding energy similar to that of 3D perovskites.

To experimentally achieve low-dielectric-confined 2D perovskites, we used EA to form the organic layers (inset I of Fig. 1c). EA has a dielectric constant as high as 37.7²¹, because of the charge dipole induced by hydroxy group and short carbon chain (Fig. 1a). We confirmed the bulk single crystal of the 2D_EA perovskites by single crystal X-ray diffraction (SCXRD) (see Methods). For comparison purposes, we also conducted measurements on $(C_6H_5(CH_2)_2NH_3)_2PbI_4$ (2D_PEA perovskites) single crystal (inset II of Fig. 1c), a conventional and widely used 2D perovskites^{5,9,11,22,23}. Temperature-dependent PL measurements were performed on both 2D EA and 2D PEA perovskite single crystals to determine the exciton-binding energies. The PL intensity of the 2D_EA perovskites dropped rapidly as the temperature increases from 50 to 160 K (Fig. 2a), indicating that the attractive force between electron and hole in the exciton is extremely weak because of the strong screening effect (inset of Fig. 2a). Meanwhile the PL intensity of the



Fig. 1 Exciton-binding energy and Bohr radius. Schematic diagram of the **a** HOCH₂CH₂NH₃⁺ (EA) molecule and **b** C₆H₅(CH₂)₂NH₃⁺ (PEA) molecules. The large charge dipole caused by the O-H bond in EA is illuminated. **c** The exciton-binding energy and Bohr radius as a function of organic-group dielectric constant in 2D perovskites as predicted by the image charge model. Calculated exciton-binding energies and Bohr radii of PEA (square) and EA (diamond) based 2D perovskites are indicated. Inset (**I**): Lattice structures of (HOCH₂CH₂NH₃)₂PbI₄ (2D_EA perovskites) and (**II**): (C₆H₅(CH₂)₂NH₃)₂PbI₄ (2D_PEA perovskites)



Fig. 2 Optical properties. Temperature-dependent photoluminescence (PL) of **a** (HOCH₂CH₂NH₃)₂PbI₄ (2D_EA) and **b** (C_6H_5 (CH₂)₂NH₃)₂PbI₄ (2D_PEA) perovskite single crystals. **c** Exciton dissociation rate extracted from temperature-dependent photoluminescence quantum efficiency (PLQE) in both 2D_EA and 2D_PEA perovskites. **d** Absorption of 2D_EA and 2D_PEA perovskites

2D_PEA perovskites showed a much slower decreasing rate as the temperature increased (Fig. 2b), indicating a more stable bound state for the excitons (inset of Fig. 2b). Integrated PL intensity was calculated (Supplementary Figure 1) and Arrhenius equation fitting (see Methods) was used to determine the thermal dissociation ratio of the samples (Fig. 2c), obtaining a binding energy for 2D_EA perovskites of ~13 meV and for 2D_PEA perovskites of ~250 meV. We also measured the absorption of the micron-size flakes of these two 2D perovskites (see Methods), and in 2D_PEA sample the exciton peak is prominent, while in 2D_EA the exciton peak is absent (Fig. 2d), indicating that the exciton-binding energy in the 2D_EA perovskites is much lower than that in 2D_PEA, which agrees with the temperaturedependent PL measurements. The exciton-binding energy of the 2D_EA perovskites is as low as that of 3D perovskites, and one order-of-magnitude smaller than the lowest reported binding energy of conventional 2D perovskites¹⁹, making thermally activated exciton dissociation to free carriers much more effective than that for conventional 2D perovskites²⁴.

To explore the exciton dissociation and free carrier generation processes in photoactive materials, different experimental and theoretical approaches can be employed. Femtosecond transient absorption spectroscopy (fs-TA) is one of the most robust and convenient choices^{25,26}. To directly access the free carrier generation and recombination, we performed fs-TA measurements on the 2D perovskite single crystals following 330 nm optical excitation (details see Methods). Figure 3a, b show the TA spectra of the 2D_EA and 2D_PEA perovskites, respectively, following 330 nm excitation. As can be seen, in addition to the strong ground state bleaching (GSB) at 515 and 500 nm for the 2D_EA and 2D_PEA perovskites, respectively, there was also a broad excited-state absorption extending over the range of 530-750 nm. More specifically, we noted a high intense photoinduced absorption (PA) and low intense broad PA that extended to the NIR region. The high and low PA signals can be attributed to hot and free charge carriers, respectively. Interestingly, we found the broad photo-induced absorption intensity due to free carriers was three-times higher for 2D_EA (inset Fig. 3a) compared with 2D_PEA (inset Fig. 3b), demonstrating the more efficient exciton dissociation in 2D_EA perovskites due to their lower exciton-binding energy. The kinetic traces of GSB recovery and photo-induced absorption of both materials are shown in Fig. 3c, d. The dynamics of GSB recovery in the 2D_EA perovskites (Fig. 3c) shows two components, a fast 65.3 ± 4 ps and long 454.3 ± 26 ps. Similarly, the photo-induced absorption of the 2D_EA perovskites shows two components of 66.8 ± 4.5 and 501.0 ± 28 ps. On the other hand, the GSB recovery and photoinduced absorption of the 2D_PEA perovskites (Fig. 3d) show also two components of 7.4 ± 0.5 , 92 ± 6 and 8.1 ± 0.6 , 96 ± 6 ps, respectively. Being in this regime, it is well known that the carrier lifetime decreases (fast electron/hole recombination) as the exciton-binding energy increases. In addition, the exciton dissociation and separation increase, which leads to free carriers, as the exciton-binding energy decreases. To show the clear change in the TA results of 2D_EA and 2D_PEA, we plotted the normalized bleach recovery kinetics and the excited state decay (Supplementary Figure 2) following 330 nm optical excitation. As can be seen from the kinetic traces, GSB recovery and the excited state decay of EA is much slower than PEA, providing clear experimental evidence for the lower exciton-binding energy in the 2D_EA perovskites. The slow GSB recovery and excited state decay results are consistent with our exciton-binding energy



Fig. 3 Charge carrier dynamics. Femtosecond transient absorption (fs-TA) spectra at different time delays following 330 nm laser excitation of the a 2D_EA and b 2D_PEA perovskites. Inset shows magnified TA spectra in 550-750 nm spectral range. Kinetic traces of the c 2D_EA and d 2D_PEA perovskites, monitored at the ground state bleaching (GSB) maxima (red, 515 and 500 nm) and at 740 nm (blue), respectively. The amplitude of the TA signals of both cases are rescaled with respect to GSB intensity

findings, and strongly prove that the 2D_EA perovskites have a longer carrier lifetime and more efficient exciton dissociation than the 2D_PEA perovskites.

Electronic/opto-electronic transport properties. Carrier mobility is another important factor that affects the device performance of perovskites. In conventional 2D perovskites, the strong quantum confinement is known to be associated with carrier mobility that is two orders-of-magnitude lower than that of 3D perovskites¹⁷. But the fact that dielectric confinement is another important origin of such low carrier mobility is rarely discussed. A low dielectric constant of the organic layer will reduce the screening effect of charge impurities, leading to a large scattering cross-section and thus short relaxation time for charge carriers²⁷. According to the Drude model, mobility $\mu = e\tau/m$ (τ is the relaxation time of scattering, e is the charge of one electron, and *m* is the effective mass of carriers), shorter scattering relaxation time results in smaller mobility. Meanwhile, in 2D_EA perovskites, Time-of-Flight (TOF) measurements showed that the carrier mobilities are ~11.1 and 9.5 cm² V⁻¹ s⁻¹ for electron and hole, respectively (Fig. 4a), and the average Hall mobility was determined to be $\sim 30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (hole mobility). The carrier mobility in the 2D_EA perovskites demonstrated here is much larger than that reported in conventional 2D perovskites^{17,22}. According to the density functional theory (DFT)-based band structure calculations (see Supplementary Note 3 and Supplementary Figure 3), the effective mass of carriers in the 2D_EA perovskites is similar to that in conventional 2D perovskites (Supplementary Table 1), therefore, we attribute the largely improved mobility of the 2D_EA perovskites to the increased

relaxation time caused by the enhanced screening effect that results from the high dielectric constant of the organic layers²⁷.

Due to the low-binding energy and high carrier mobility, the 2D_EA perovskites are expected to present much better photoexcited carrier extraction efficiency compared to conventional 2D perovskites in terms of photoresponsivity, photo gain, and using response time. As shown in Fig. **4**b, а metal-semiconductor-metal (MSM) structure based on 2D_EA perovskite single crystals, we were able to achieve ~10-times higher photoresponsivity than that based on 2D_PEA over a wide range of incident wavelengths from 360 to 600 nm. As shown in Fig. 4c, the photo gain of the 2D_EA perovskites is also one order-of-magnitude higher than that of the 2D_PEA perovskites (we chose incident wavelengths of 550 nm for the 2D_EA perovskites, and 530 nm for the 2D_PEA perovskites to achieve their best photo gains, respectively). The photo gain is proportional to $\mathcal{C}_1/\mathcal{C}_t$, where \mathcal{C}_1 and \mathcal{C}_t are carrier lifetime and carrier transit time, respectively²⁸. \mathcal{C}_1 in 2D_EA perovskites is large because excitons are easily dissociated to free carriers, which reduces the probability of recombination. \mathcal{L}_{t} is defined by $d^2/V\mu$, in which d is channel length (the distance between two electrodes in the perovskite MSM structures), V is the applied bias voltage, and μ is the carrier mobility. We found that the longer carrier lifetime and larger carrier mobility of the 2D_EA perovskites resulted in a much larger photo gain than that in the 2D_PEA perovskites. The photoelectric response time is another critical parameter for evaluating the photo-excited carrier extraction efficiency. We selected a bias voltage of 3 V as it exceeds the saturation voltage (Fig. 4c), and achieved rise and decay times of 53.4 and 57.2 µs, respectively, in 2D_EA (Fig. 4d),



Fig. 4 Optoelectronic properties and carrier transport. **a** Linear fit of transit time versus inverse voltage V⁻¹ of the 2D_EA perovskites in Time-of-Flight measurements. Error bars were estimated from the standard deviation of repeated measurements. **b** Wavelength-dependent photoresponsivity of 2D_EA and 2D_PEA perovskites under 10 W m⁻² power density at 3 V bias voltage. **c** Photogain of 2D_EA and 2D_PEA and under 5 W m⁻² power density at 550 and 530 nm light, respectively. **d** The transient photoresponse of 2D_EA and (inset) 2D_PEA single crystal perovskites under 5 W m⁻² power density at 550 and 530 nm light, respectively

which is ~2 order-of-magnitude lower than that of 2D_PEA (3.78 and 4.30 ms for rise and decay time as shown in the inset of Fig. 4d). Generally, the response time is proportional to the carrier transit time in semiconductors, and photo-excited carrier transfer time at the semiconductor/metal interface. Because the carrier transit time is inversely proportional to the carrier mobility²⁹, the carrier transit time in the device of the 2D_EA perovskites is ~1 order-of-magnitude smaller than that in 2D_PEA perovskites. As a result, the photo-excited carrier extraction time in the 2D_EA perovskite/metal interface is much faster than that in 2D_PEA perovskite/metal interface. To sum up, based on the results of photoresponsivity, photo gain, and response time we conclude that due to the low binding energy and high carrier mobility, the 2D_EA perovskite show signficantly improved carrier extraction efficiency, which could have a huge impact on the optoelectronic device performance, particularly for solar cells and photodetectors. Further optimization of device fabrication implementing the 2D_EA perovskite in the devices is needed and currently under investigation.

Our method of reducing the dielectric constant in 2D perovskites can be generalized in several aspects. For example, if the halogen I atom is replaced by Br to synthesize EA_2PbBr_4 , a similarly low exciton-binding energy can be achieved (Supplementary Figure 4). As shown in Supplementary Figure 5, the ratio of I and Br can even be tuned to achieve color-tuning PL. Furthermore, as discussed earlier, reducing the dielectric

confinement by inserting high dielectric-constant organic layers can be combined with reducing quantum confinement by increasing the thickness of the inorganic PbI layer to achieve further decrease of the exciton-binding energy and increase of mobility^{17,27}.

Stability in moisture. In addition to optoelectronic properties, stability under humidity is a crucial metric for photovoltaics and one of the major obstacles for the commercial adoption of perovskite-based photovoltaic technologies^{5,6}. A variety of technological methods have been proposed to address the instability problem, including an "intrinsic" method of utilizing the hydrophobic properties of the organic components to prevent the perovskite framework from the direct exposure to moisture, and an "extrinsic" method performed by an encapsulation technique in which the polycrystalline thin film can be protected by the transportation layers⁶. In this report, we focus on 2D perovskite single crystals without any transportation layer so that we can get insight into the "intrinsic" humidity stability related to the organic layers only. We measured the time-dependent photoresponsivity of MSM device fabricated in the 2D_EA and 2D_PEA perovskite single crystals after they were exposed to an environment of 60% relative humidity (RH) and 20 °C temperature. As shown in Fig. 5a, the photoresponsivity of the 2D_PEA MSM device started to decrease in a few hours (e.g. a 30% decrease after 48 h). The 2D_EA MSM device showed much



Fig. 5 Humidity stability. **a** Normalized time-dependent responsivity of the 2D_EA and 2D_PEA perovskites. **b** Schematic diagram of hydrogen bonds between the organic layers in the 2D_EA perovskites

better stability and remained at ~90% photoresponsivity after 5 days relative to its starting value. Our results indicate that the 2D_EA perovskites can lead to a much better humidity resistance than conventional 2D perovskites.

To prove the enhanced humidity stability of the 2D_EA single crystal, time-dependent XRD (TDXRD) was measured. The TDXRD of the 2D_EA single crystal does not show any indication of degradation after 20 days exposed in 60% RH at 20 °C. On the other hand, the TDXRD of the 2D_PEA perovskites shows a new peak attributed to PbI₂ after only one day exposed to 60% RH at 20 °C (Supplementary Figure 6). To gain further insight into the excellent stability of the 2D_EA perovskites, time-dependent X-ray photoelectron spectroscopy (XPS) of the Pb 4*f* region was measured on 2D_EA single crystals to test the degradation as a function of exposure time in a 60% RH, 20 °C environment. In Supplementary Figure 7, the peaks at 137.9 and 142.5 eV, corresponding to the binding energy of Pb 4*f*_{7/2} and Pb 4*f*_{5/2} of Pb-I in the 2D_EA single crystal, do not show any indication of degradation after 6 days exposure. To evaluate the

chemical composition of the surface, we recorded XPS at 360 eV incidence photon energy, corresponding to a mean-free path (for the outgoing ~220 eV photoelectrons) of <1 nm³⁰. The 2D_EA perovskites (Supplementary Figure 8) was unchanged over 6 days without any indication of a PbI₂ or Pb⁰ peak. These XRD and XPS results confirmed the outstanding humidity stability of 2D_EA perovskites as shown in time-dependent photoresponsivity results. We attribute the remarkable enhancement of this stability to the strong hydrogen bonding between the organic layers (Fig. 5b) compared to that in the 2D_PEA crystal (where London dispersion forces primarily dominate), enabling the hydrophilic organic groups to restrict the penetration of water and oxygen more effectively.

Discussion

In summary, we have investigated the effect of the organic layer with different dielectric constants on the exciton-binding energy and carrier mobility in 2D perovskites. We found that the dielectric confinement effect can be significantly tuned by inserting different dielectric-constant organic layers between the inorganic Pb-I units. To investigate this concept, we compared two different kinds of 2D perovskites, one that is highly dielectricconfined and the other that has extremely low dielectric confinement. We have shown that in the low dielectric-confined 2D perovskites the exciton-binding energy is ~13 meV, which is 20 times smaller than that in the high dielectric-confined 2D perovskites. Moreover, in the low dielectric-confined 2D perovskite single crystal we demonstrated excellent photo-excited carrier extraction efficiency due to the largely improved carrier mobility and reduced exciton-binding energy, and outstanding moisture resistance due to the strong hydrogen bonding between the organic layers. Based on these findings, we believe the lowdielectric-confined 2D perovskites might provide an alternative way to improve the performance of hybrid perovskite-based optoelectronics.

Method

Synthesis of perovskite single crystals. 2D_EA and 2D_PEA single crystals were grown using a cooling method. To synthesize the 2D_EA single crystal, 0.160 g PbI₂ was dissolved in 2 ml of 57% HI in a sample vial. Thereafter, 0.080 g $HOC_2H_4NH_2$ was added and the precipitate dissolved by sonication at room temperature. The solution was then cooled down to 4 °C.

X-Ray structure analysis. Single-crystal intensity data were collected using a Bruker APEX DUO with MoK_{α} radiation (wavelength 0.71073 Å) at 100 K. The cif files of 2D_EA perovskites are upload to CCDC database, as shown in Data availability.

The crystallographic plane of the large single crystal was probed using a Bruker D8 Venture SCXRD Cu target. After the small piece was checked, the

crystallographic plane of the centimeter-sized single crystal could be deduced. Powder X-ray diffraction was carried out using a Bruker D8 Advance powder XRD with Cu Ka radiation and a low-angle kit.

Temperature-dependent PL. The temperature-dependent PL measurements were performed at the Semiconductor and Material Spectroscopy lab at KAUST. The samples were initially cooled to cryogenic temperatures using a closed-cycle He cryostat supplied by the ARS Laboratory. Prior to cooling, the samples were placed under high vacuum (10^{-6} mTorr). A HeCd laser emitting at a wavelength of 325 nm was used as the PL excitation source. The PL emissions of the samples were collected using an Andor Shamrock 303i spectrograph with a UV–VIS grating of 299 mm⁻¹ and a blaze wavelength of 300 nm. The spectra were subsequently recorded digitally, using a thermoelectrically cooled electron multiplying CCD sensor by Andor.

Arrhenium formula simulation of the binding energy. We assume that photo generated excitons are only depopulated by thermal dissociation and radiative recombination³¹. In the steady-state PL measurement, we have

$$n_{\rm pg} = n_{\rm PL} + n_{\rm td}$$

in which n_{pg} refers to the number of photo-generated excitons, n_{PL} is the number

of the radiative emissions induced by the exciton recombination (which can be determined from the integrated PL intensity), and $n_{\rm td}$ is the number of thermally dissociated excitons. When *T* is not too high for $n_{\rm td}$ to saturate, according to the Arrhenium formula, we have $n_{\rm td} \propto A e^{-E_{\rm b}/kT}$, in which $E_{\rm b}$ is the binding energy and *k* is the Boltzmann constant. Assuming that when $T = \infty$ it has $n_{\rm PL} = 0$, then we have

$$n_{\rm PL} = n_{\rm pg} - n_{\rm td} = A \left(1 - e^{-E_{\rm b}/kT} \right)$$

After fitting $n_{\rm PL}(T),$ we can determine A and $E_{\rm b}.$ Finally the thermal dissociation ratio (T.D.R.) is

T.D.R. =
$$e^{-E_{\rm b}/kT} = 1 - \frac{n_{\rm PL}}{A}$$

We also did TDXRD of 2D_EA and 2D_PEA perovskites (Supplementary Figure 9) to exclude the phase transition within the range of the temperature we selected for integrated PL fitting.

Absorption measurement. Two measurements were performed to collect the absorption spectra for the 2D perovskite nanosheets. In the first measurement, the absolute values of reflection and transmission at a wavelength of 514.5 nm (Ar ion laser) were measured for the extraction of the absorption value using a lock-in amplifier coupled with a silicon photodiode. Absorption spectra of arbitrary intensity were obtained using a supercontinuum laser (Fianium WhiteLase SC-400). The reflection/transmission light was analyzed by a spectrometer to produce the spectra. In those measurements, the laser was focused by a ×50 objective. For reflection measurement, the reflected light was collected through the same objective. For transmission measurement, the transmitted light was collected using a ×20 objective. The system was calibrated using quartz substrate and a silver mirror as the reference for transmission and reflection, respectively.

Femtosecond transient absorption measurement. Transient absorption (TA) spectroscopy was performed at timescales of 0.1 ps to 6 ns using a regeneratively amplified Ti:sapphire laser (800 nm laser pulses of 35 fs pulse width having a 1 kHz repetition rate), and in conjunction with EOS spectrometers. The excitation pump pulses at 330 nm were generated after passing through a fraction of the 800 nm beam into the spectrally tunable (240-2600 nm) optical parametric amplifier (Newport Spectra-Physics). The pump fluence of the excitation laser source was adjusted by using a neutral density filter to avoid multiple charge carrier generation. The probe pulses (UV-visible and NIR wavelength continuum, white light) were generated by passing another fraction of the 800 nm pulses through a 2-mmthick calcium fluoride (CaF₂) crystal. Before white light generation the 800 nm amplified pulses were passed through a motorized delay stage. Depending on the movement of the delay stage, the transient species were detected following excitation at different time scales. The white light was split into two beams (named as signal and reference) and focused on two fiber optics for an improved signal-tonoise ratio. The excitation pump pulses were spatially overlapped with the probe pulses on the samples after passing through a synchronized mechanical chopper (500 Hz) which blocked alternative pump pulses. The absorption changed (ΔA) was measured with respect to the time delay and wavelength. All spectra were averaged over a time period of 2 s for each time delay. Our experimental fs-TA setup is detailed elsewhere³².

Fabrication of 2D perovskite MSM junctions. We chose gold to fabricate the metal electrodes in order to measure the 2D_EA and 2D_PEA MSM junctions after we considered the work functions (Supplementary Figure 10) of the 2D perovskites obtained from photo-electron spectroscopy in air. Moreover, to measure the samples and investigate the electron transport in the in-plane direction (Supplementary Figure 11b), powder X-ray diffraction was performed to check the crystallographic plane. After checking the crystallographic plane, we cleaved the surface of the sample to exclude interference from any surface defects or trap (Supplementary Figure 11a). A shadow mask for depositing 500-µm-wide electrodes with 20-µm channel length was taped to the cleaved crystallographic plane and 60-nm-thick gold was deposited with an electron gun evaporator (0.6 Å s⁻¹, 10^{-6} Tor). Finally, the MSM structures were fabricated within one hour in vacuum after the perovskite crystal was prepared, and we finished the measurements in two hours.

Electrical characterization/optical testing.

 Electrical properties were measured using a Keithley 4200-SCS parameter analyzer with a Keithley 4210-PA and a Cascade CM300 probe station. A Newport 1000 W Xenon Lamp 66921 light source with a Newport monochromator was used for the responsivity measurements. To confirm the size and uniform intensity distribution of the incident light spot, the optical profile was measured by a beam profiling camera (Ophir Spiricon silicon CCD camera SP620U) and the power at each wavelength was measured using a calibrated photodiode (Newport 818-UV). MSM junctions were excited by a uniformly distributed intensity spot ($3080 \,\mu\text{m} \times 1167 \,\mu\text{m}$) and the responsivity *R* was calculated using the following formula:

$$R = \frac{I_{\text{photo}} - I_{\text{dark}}}{\text{Power illumination in active area}}$$

in which $I_{\rm photo}$ and $I_{\rm dark}$ are the currents under photoexcitation and in the dark, respectively. The active area of the sample was 20 μm (distance between two electrodes) \times 500 μm (width of electrodes).

- 2. Hall mobility was measured with an HMS-3000 Hall measurement system.
- 3. The time-of-fight (TOF) setup is shown in Supplementary Figure 12a. The TOF result of the 2D_EA perovskites is shown in Supplementary Figure 12b. However, in the 2D_PEA perovskites the diffusion length is too short due to the strong dielectric confinement, so we were unable to obtain the carrier mobility in 2D_PEA perovskites by the TOF measurement.

Synchrotron XPS. The energy-dependent synchrotron XPS measurements were performed at the Stanford Synchrotron Radiation Lightsource (Stanford, CA, US) at beamline 8-2. The beamline was equipped with a SGM monochromator, operated using a 500 mm⁻¹ rating at an energy resolution of ~0.5 eV The samples were loaded onto an aluminum stick, attached with double-sided carbon tape, and all the measurements were done in one single load below 10⁻⁸ Torr. The photoelectrons were analyzed with a cylindrical mirror analyzer, operated at 50 eV pass energy. All measurements presented here were performed at the magic angle (54.7° incidence). The spectrometer was calibrated to Au_{4f} = 84 eV and the spectra were internally calibrated using the carbon peak to take into account some charging that was observed.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request. The X-ray crystallographic coordinates for the structure reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number 1869720 for (HOCH₂CH₂NH₃)₂PbI₄, and 1869719 for (HOCH₂CH₂NH₃)₂PbBr₄. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: 27 July 2018 Accepted: 10 October 2018 Published online: 15 November 2018

References

- Lee, M. M., Teuscher, J., Miyasaka, T., Murakami, T. N. & Snaith, H. J. Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. *Science* 338, 643–647 (2012).
- Burschka, J. et al. Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature* 499, 316 (2013).
- Jeon, N. J. et al. Compositional engineering of perovskite materials for highperformance solar cells. *Nature* 517, 476–480 (2015).
- Zhou, H. et al. Interface engineering of highly efficient perovskite solar cells. Science 345, 542–546 (2014).
- Smith, I. C., Hoke, E. T., Solis-Ibarra, D., McGehee, M. D. & Karunadasa, H. I. A layered hybrid perovskite solar-cell absorber with enhanced moisture stability. *Angew. Chem. Int. Ed.* **126**, 11414–11417 (2014).
- Tsai, H. et al. High-efficiency two-dimensional Ruddlesden-Popper perovskite solar cells. *Nature* 536, 312–316 (2016).
- Dohner, E. R., Jaffe, A., Bradshaw, L. R. & Karunadasa, H. I. Intrinsic whitelight emission from layered hybrid perovskites. *J. Am. Chem. Soc.* 136, 13154–13157 (2014).
- Dou, L. et al. Atomically thin two-dimensional organic-inorganic hybrid perovskites. *Science* 349, 1518–1521 (2015).
- Ma, D. et al. Single-crystal microplates of two-dimensional organic-inorganic lead halide layered perovskites for optoelectronics. *Nano Res.* 10, 2117–2129 (2017).
- Yang, W. S. et al. High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. Science 348, 1234–1237 (2015).
- 11. Yang, S. et al. Ultrathin two-dimensional organic-inorganic hybrid perovskite nanosheets with bright, tunable photoluminescence and high stability. *Angew. Chem. Int. Ed.* **56**, 4252–4255 (2017).
- Yaffe, O. et al. Excitons in ultrathin organic-inorganic perovskite crystals. *Phys. Rev. B* 92, 045414 (2015).
- Hanamura, E., Nagaosa, N., Kumagai, M. & Takagahara, T. Quantum wells with enhanced exciton effects and optical non-linearity. *Mater. Sci. Eng.: B* 1, 255–258 (1988).
- Hong, X., Ishihara, T. & Nurmikko, A. Dielectric confinement effect on excitons in PbI 4-based layered semiconductors. *Phys. Rev. B* 45, 6961 (1992).
- Ishihara, T., Takahashi, J. & Goto, T. Exciton state in two-dimensional perovskite semiconductor (C₁₀H₂₁NH₃) 2PbI₄. *Solid State Commun.* 69, 933–936 (1989).

ARTICLE

- Pedesseau, L. et al. Advances and promises of layered halide hybrid perovskite semiconductors. ACS Nano 10, 9776–9786 (2016).
- Milot, R. L. et al. Charge-carrier dynamics in 2D hybrid metal-halide perovskites. *Nano. Lett.* 16, 7001–7007 (2016).
- Blancon, J.-C. et al. Extremely efficient internal exciton dissociation through edge states in layered 2D perovskites. *Science* 355, eaal4211 (2017).
- Smith, M. D. et al. Decreasing the electronic confinement in layered perovskites through intercalation. *Chem. Sci.* 8, 1960–1968 (2017).
- Mercier, N. et al. Unique hydrogen bonding correlating with a reduced band gap and phase transition in the hybrid perovskites (HO(CH₂)₂NH₃)₂PbX₄ (X = I, Br). *Inorg. Chem.* 43, 8361–8366 (2004).
- Covington, A. K., Dickinson, T. Physical chemistry of organic solvent systems. Plenum: New York, 1973.
- 22. Kagan, C., Mitzi, D. & Dimitrakopoulos, C. Organic-inorganic hybrid materials as semiconducting channels in thin-film field-effect transistors. *Science* **286**, 945–947 (1999).
- 23. Mitzi, D. B. et al. Hybrid field-effect transistor based on a low-temperature melt-processed channel layer. *Adv. Mater.* 14, 1772–1776 (2002).
- Savenije, T. J. et al. Thermally activated exciton dissociation and recombination control the carrier dynamics in organometal halide perovskite. *J. Phys. Chem. Lett.* 5, 2189–2194 (2014).
- Begum, R. et al. Engineering interfacial charge transfer in CsPbBr₃ perovskite nanocrystals by heterovalent doping. J. Am. Chem. Soc. 139, 731–737 (2016).
- Zhang, Y. et al. Direct-indirect nature of the bandgap in lead-free perovskite nanocrystals. J. Phys. Chem. Lett. 8, 3173-3177 (2017).
- 27. Ma, N. & Jena, D. Charge scattering and mobility in atomically thin semiconductors. *Phys. Rev. X* 4, 011043 (2014).
- 28. Konstantatos, G. et al. Ultrasensitive solution-cast quantum dot photodetectors. *Nature* **442**, 180 (2006).
- Lopez-Sanchez, O., Lembke, D., Kayci, M., Radenovic, A. & Kis, A. Ultrasensitive photodetectors based on monolayer MoS₂. *Nat. Nanotechnol.* 8, 497–501 (2013).
- Li, W., Li, J., Niu, G. & Wang, L. Effect of cesium chloride modification on the film morphology and UV-induced stability of planar perovskite solar cells. J. Mater. Chem. A 4, 11688–11695 (2016).
- Chen, Z. et al. Photoluminescence study of polycrystalline CsSnI₃ thin films: Determination of exciton binding energy. J. Lumin. 132, 345–349 (2012).
- 32. Shi, D. et al. Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals. *Science* **347**, 519–522 (2015).

Acknowledgements

This work was financially supported by the King Abdullah University of Science and Technology (KAUST) Office of Sponsored Research (OSR-2016-CRG5-3005), KAUST solar center (FCC/1/3079-08-01), and KAUST baseline funding. Optical absorption characterization was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under contract no. DE-AC02-05CH11231 within the Electronic Materials Program (KC1201).

Author contributions

B.C., T.Y.L., and J.H.H. conceived the idea. B.C. calculated the exciton-binding energy. T. Y.L. and B.C. synthesized the materials and fabricated the device. T.Y.L., B.C., K.T.H., R. Z.L., and C.H.L. designed and performed the optoelectronic and electrical measurements. I.A.A. and I.S.R. performed temperature-dependent PL measurements. P.M. and O.F.M. designed and performed the femtosecond transient absorption measurements. X.M. and T.Y.L. arranged and analyzed the XRD experimental data. D.H.L. and A.J. did the absorption measurement. T.Y.L., D.N., and S.D. arranged and analyzed the synchrotron XPS experimental data. J.Y. and O.F.M. calculated the band structure. B.C., T.Y.L., P.C. W., and J.H.H. analyzed the data and wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information

Supplementary information accompanies this paper at https://doi.org/10.1038/s42005-018-0082-8.

Competing interests: The authors declare no competing interests.

Reprints and permission information is available online at http://npg.nature.com/ reprintsandpermissions/

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/ licenses/by/4.0/.

© The Author(s) 2018