

DOI: 10.1002/((please add manuscript number))

Article type: Communication

Title: Efficient and Layer-dependent Exciton Pumping Across Atomically-thin Organic-Inorganic Type-I Heterostructures

Linglong Zhang, Ankur Sharma, Yi Zhu, Yuhan Zhang, Bowen Wang, Miheng Dong, Hieu Nguyen, Zhu Wang, Bo Wen, Yujie Cao, Boqing Liu, Xueqian Sun, Jiong Yang, Ziyuan Li, Arara Kar, Yi Shi, Daniel Macdonald, Zongfu Yu, Xinran Wang, Yuerui Lu**

Dr. L. Zhang, Y. Zhang, Y. Cao, Prof. Y. Shi, Prof. X. Wang

National Laboratory of Solid State Microstructures, Collaborative Innovation Center of Advanced Microstructures, School of Electronic Science and Engineering, Nanjing University, Nanjing 210093, People's Republic of China

Dr. L. Zhang, A. Sharma, Y. Zhu, B. Wang, M. Dong, H. Nguyen, B. Wen, B. Liu, X. Sun, J. Yang, A. Kar, Prof. D. Macdonald, Associate Prof. Y. Lu.

Research School of Engineering, College of Engineering and Computer Science, the Australian National University, Canberra, Australian Capital Territory 2601, Australia.

Dr. Z. Wang, Z. Yu

Department of Electrical and Computer Engineering, University of Wisconsin, Madison, WI 53706, USA

Dr. Z. Li

Department of Electronic Materials Engineering, Research School of Physics and Engineering, the Australian National University, Canberra 2601, ACT, Australia

*E-mail: Yuerui Lu (yuerui.lu@anu.edu.au) and Xinran Wang (xrwang@nju.edu.cn)

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version of Record](#). Please cite this article as [doi: 10.1002/adma.201803986](https://doi.org/10.1002/adma.201803986).

This article is protected by copyright. All rights reserved.

Keywords: (two-dimensional material, exciton pumping, Organic-inorganic, Type-I heterostructure, binding energy)

Abstract:

The fundamental light-matter interactions in monolayer transition metal dichalcogenides might be significantly engineered by hybridization with their organic counterparts, enabling intriguing opto-electronic applications. Here, we fabricated atomically thin organic-inorganic (O-I) heterostructures, comprising of monolayer MoSe₂ and mono-/few-layer single-crystal pentacene samples. These heterostructures show type-I band alignments, allowing the efficient and layer-dependent exciton pumping across the O-I interfaces. The interfacial exciton pumping has much higher efficiency (>86 times) than the photoexcitation process in MoSe₂, although the pentacene layer has much lower optical absorption than MoSe₂. This highly enhanced pumping efficiency is attributed to the high quantum yield in pentacene and the ultra-fast energy transfer between the O-I interface. Furthermore, those organic counterparts significantly modulate the bindings of charged excitons in monolayer MoSe₂ *via* their precise dielectric environment engineering. Our results open new avenues for exploring fundamental phenomena and novel optoelectronic applications using atomically thin O-I heterostructures.

Van der Waals (vdW) heterostructures have in-plane covalently bonded atomic layers which facilitate the formation of well-defined interfaces with absence of any dangling bonds.^[1] The constituent layers interact weakly with out of plane layers and this weak vdW interaction enables the stacking of atomically thin layers on each other with precision. Semiconducting transition metal dichalcogenides (TMDCs) are important building blocks for fabricating two-dimensional (2D) vdW heterostructures that possess atomically sharp interfaces, enabling promising optoelectronic

This article is protected by copyright. All rights reserved.

applications such as efficient photodetectors, light emitting diodes, resonant tunneling diodes and solar cells.^[2-4] Organic molecular semiconductors have also recently been integrated with 2D TMDCs to form vdW heterostructures,^[5-10] which can dramatically engineer the light-matter interactions in the hybrid system and allow for new types of optoelectronic devices. However, those organic counterparts reported were based on bulk organic materials (more than 20 nm thick). The organic molecular arrangements on those reported O-I interfaces were not well controlled on the atomic scale, although the opto-electronic properties of organic molecular crystals are typically very sensitive to its aggregation and molecular arrangements.^[11-13] Compared to their bulk counterparts, our recently reported atomically thin high-quality 2D organic molecular crystals possesses well-defined molecular arrangements and the interesting layer-dependent carrier transport properties.^[14,15] This will allow us to build atomically thin O-I interfaces with well-controlled molecular arrangements on the interface and explore how the molecular aggregations would affect the light-matter interactions in the hybrid system. Furthermore, ultra-thin organic molecular crystals have a clear interface and high excitonic densities with high binding energies,^[16] which can comprehensively interact with excitonic states in the inorganic 2D materials and can lead to various applications for optical devices such as light emitting devices.^[17-19]

Here, we demonstrated atomically thin O-I heterostructures, by stacking exfoliated monolayer MoSe₂ onto mono-/few-layer single-crystal pentacene samples that were epitaxially grown over h-BN surfaces. We observed significant photoluminescence (PL) enhancement from the monolayer MoSe₂ and PL quenching in the pentacene layers. Photoluminescence exciton (PLE) measurements were used to prove the type-I band alignments. The atomically thin O-I heterostructures with well-controlled interfacial molecular arrangements and type-I band alignments allow us to study the

efficient and layer-dependent exciton pumping across the high-quality O-I interfaces which is in contrast to previously reported O-I heterostructures^[5,6,14,20,21] (with type-II band alignments). The interfacial exciton pumping efficiency from the hybridization of a wetting layer pentacene (0.5 nm thick) was measured to be ~86 times higher than that from the photoexcitation process in MoSe₂, although the pentacene layer has much lower optical absorption than MoSe₂. The highly enhanced pumping efficiency is attributed to the high quantum yield in pentacene and the ultra-fast energy transfer between the O-I interface. The measured interfacial pumping efficiency was sensitive to the layer number of organic 2D materials. Moreover, compared with other substrates, such as SiO₂ and h-BN, the pentacene layer has highly reduced dielectric screening effect on the many-body interactions in MoSe₂, which resulted in the enhanced bindings of the charged excitons in monolayer MoSe₂ depending on the spacing thickness of pentacene layer.^[22] Our findings provide a new way to engineer the light-matter interactions in atomically thin semiconductors and their hybrids, enabling various new optoelectronic devices, such as ultrathin lighting diodes, heterostructure lasers, *etc.*

Figure 1a shows the schematic configuration of the heterostructure. Firstly, few-layers of h-BN were mechanically exfoliated onto a 290 nm Si/SiO₂ substrate. Then the ultra-thin 2D pentacene films were subsequently grown on the exfoliated h-BN *via* the physical vapor deposition (PVD) method in a tube furnace. The growth process is detailed in the author's previous work.^[14] MoSe₂ monolayer was then exfoliated and stacked on the atomically thin pentacene layers to form the heterostructures.^[23] This technique is a better method to avoid contamination and damage of the organic materials during the transfer process, and achieves ultra-clean and intact atomic interfaces.^[24] Figure 1b and 1c show the optical microscope images of before and after transfer of monolayer MoSe₂ onto the pentacene film, respectively. The interfacial layer of pentacene grown

directly over the h-BN is referred to as the Wetting layer (WL) and subsequent layers above the WL are referred to as 1L and 2L.^[14] After heterostructure, all individual heterostructures are characterized by Raman spectroscopy after stacking (see Figure S1) to confirm the formation of heterostructure. AFM microscopy (Figure 1d and Figure S2) was further used to deterministically designate each pentacene layer based on the observed thickness. Three different heterostructures based on the thickness of pentacene layers underneath the monolayer MoSe₂ were fabricated. The optical image after stacking shown in Figure 1c shows three distinct heterostructure regions. PL spectroscopy is a sensitive probe to study the dynamic interlayer and intralayer charge transfer excitonic states which can provide evidence of coupling between the individual heterostructure layers.^[2,24,25] The PL spectra of the various heterostructures are shown in Figure 1e, an excitonic peak around 788 nm was observed for MoSe₂ (olive curve) and pentacene showed a broad emission in the range of 550–700 nm (red curve). The PL peak intensity of the 1L MoSe₂ + WL PEN heterostructure at ~788 nm clearly indicates ~2.8 times enhancement (Figure 1e I) as compared to that of monolayer MoSe₂ on SiO₂/Si substrate, whereas the PL peak from pentacene has been quenched. The enhancement factor η is defined as the ratio of absolute PL intensities of a heterostructure (HS) to that of the monolayer MoSe₂ on SiO₂/Si substrate at 788 nm as observed during the experiments (i.e., $\eta = I_{HS}/I_{MoSe_2}$). Slightly lower enhancements were observed in the 1L MoSe₂ + 1L PEN ($\eta \approx 2.4$, Figure 1e II), 1L MoSe₂ + 2L PEN ($\eta \approx 1.7$, Figure 1e III) and 1L MoSe₂ + bulk PEN ($\eta \approx 1.2$, Figure S3) heterostructures. Several devices (>5) were tested and these results were repeatable after numerous measurements. Also, we tested the heterostructures of 1L MoSe₂ on 2D pentacene after one month and the enhancement factor was observed to be stable, as compared with the initial measurements (Figure S4).

In heterostructure design, the relative band alignment is the key factor that determines the type of heterostructure.^[26] **Figure 2a** illustrates the alignment of electronic bands of pentacene and MoSe₂,^[27-29] where the MoSe₂/pentacene forms a type-I heterojunction. Specifically, the highest occupied molecular orbital (HOMO) of pentacene is lower than the valence band maximum (VB) of monolayer MoSe₂ and the lowest unoccupied molecular orbital (LUMO) of pentacene is higher than the conduction band minimum (CB) of monolayer MoSe₂. As shown in Figure 2a, photoexcited carriers would transfer from pentacene to MoSe₂ due to large inbuilt potential and combine radiatively, which leads to the enhancement of the PL intensity in the MoSe₂ layer and the quenching of the PL intensity in pentacene layer (Figure 1e).

To further confirm the type-I band alignment nature of O-I hybrid heterostructures, photoluminescence excitation (PLE) experiments at room temperature were conducted. As shown in Figure 1e, the exciton peak position of 1L MoSe₂ is ~788 nm (1.57 eV), which matches well with previous results.^[30-32] Pentacene has a broad exciton peak shape at 585 nm (2.12 eV).^[6,14] It implies that pentacene's lowest excited energy should be larger than that of monolayer MoSe₂. Figs. 2b and 2c show the PL spectra from 1L MoSe₂ and the 1L MoSe₂ + WL PEN heterostructure with excitation wavelength of 532 nm (2.33 eV) and 750 nm (1.65 eV), respectively. Figure 2b shows the PL intensity enhancement factor (η) is still around 2.8 which matches well with PL spectrum of Figure 1e. This is due to both the MoSe₂ and pentacene layers of the heterojunction were excited with an excitation energy of 2.33 eV. The photoexcited carriers can only transfer from the pentacene layer to MoSe₂ if the band alignment is type-I. Specifically, both electrons and holes are expected to transfer to MoSe₂ (see Figure 2a). In contrast, under an excitation wavelength of 750 nm as shown in Figure 2c, the PL intensity from 1L MoSe₂ + WL PEN heterostructure is comparable to that of monolayer MoSe₂ on

SiO₂/Si substrate. In this case with 750 nm excitation, only the MoSe₂ layer was excited since the lowest excitonic energy of pentacene is ~1.83 eV (Figure 1e).^[33] The PL intensity from the heterostructure was slightly higher (~1.19 times) than that from the 1L MoSe₂ sample on SiO₂/Si substrate (Figure 2c). This small PL enhancement might be due to that the pentacene layer acts as a passive layer decreasing nonradiative decay from the substrate or interface, which can be supported by the slightly increased carrier lifetime for exciton (~788 nm) peak of heterostructure than that of 1L MoSe₂ sample on SiO₂/Si (Figure S5).^[34,35] From the PLE measurement (Figure 2d), PL intensity ratio (i.e., η) decreases sharply over excitation wavelengths of 700-750 nm, which corresponding to the lowest excitonic energy band in pentacene.^[33] The PLE data clearly confirms the type-I band alignment in our 1L MoSe₂ + WL PEN heterostructure. Similar PLE measurements were conducted to confirm the type-I band alignments in 1L MoSe₂ + 1L PEN and 1L MoSe₂ + 2L PEN heterostructures as shown in Figure S6.

The type-I band alignments in our atomically thin O-I heterostructures allow the efficient exciton pumping across the O-I interfaces. The hybridization of a WL pentacene (~0.5 nm) leads to PL enhancement of 2.8 times. Considering that the WL pentacene has much lower measured optical absorption than 1L MoSe₂ (~51 times lower) at the excitation wavelength of 532 nm (see Table S1 and associated text), the exciton pumping efficiency across the O-I interface should be much higher than that from photoexcitation process in 1L MoSe₂. To further analyze the pumping efficiencies in the different heterostructures, an internal exciton pumping efficiency enhancement factor (β) is defined as:

$$\beta = \frac{\text{Exciton pumping efficiency from heterostructure}}{\text{Exciton pumping efficiency from photoexciton in TMD}} = \left(\frac{I_{HS} - I_{TMD}}{I_{TMD}} \right) \left(\frac{A_{TMD}}{A_{PEN}} \right) \quad (1)$$

where I_{HS} and I_{TMD} are the measured integrated PL intensity from the heterostructure (HS) and 1L MoSe₂ on SiO₂/Si substrate, respectively. A_{TMD} and A_{PEN} represent the measured absorption value from monolayer MoSe₂ and pentacene, respectively (Supplementary Note 3 and Table S1). The measured β values for the 1L MoSe₂ + WL, 1L MoSe₂ + 1L PEN and 1L MoSe₂ + 2L PEN heterostructures were 86.4, 20.4 and 3.2, respectively, which decrease with increasing thickness of pentacene film (Figure 3a), similar trend with the thickness-normalized PL intensities. The β values are highly related to the quantum yields (QYs) (Supplementary Note 4) and carrier lifetimes in both layers,^[36] photocarrier relaxation pathways and energy transfer channels (Figure 3b). In the 1L MoSe₂ + WL PEN heterostructure under 532 nm laser excitation, both the MoSe₂ and pentacene would be excited. The charge transfer process between O-I interfaces is typically ultrafast (6.7 ps, for instance),^[6,37,38] which is much shorter than the measured carrier lifetime in pentacene (1128 ps) and that in monolayer MoSe₂ (448 ps) (Figure 3c).^[35] Therefore, a large fraction of pentacene photo-excited charges (both electrons and holes) could transfer quickly to the MoSe₂ side and relax to some excited states for radiative recombination. Also, because WL pentacene has much higher QY and much lower optical absorption (Supplementary Note 3,4 and Table S1) than 1L MoSe₂, the interfacial exciton pumping efficiency in our atomically thin heterostructures will be much higher than that from the photoexcitation process in 1L MoSe₂, thus a high β value.

The layer-dependent β values are highly related to the layer-dependent charge transport properties in 2D pentacene.^[14] As described in our previous report,^[14] WL pentacene was not conductive owing to the absence of intralayer π - π stacking. The photo-excited electrons and holes in the WL are coupled through long-range coulombic forces (Figure 3d) and are immobile within the layer.^[14] These localized charges can move more efficiently across the interface of the

heterostructure into the MoSe₂. In 1L pentacene, charges are slightly more mobile within the pentacene layer and move through a hopping mechanism and are slightly more diffused along the pentacene layer (Figure 3e).^[14] Some charges diffuse and rest then transfer across the interface into the MoSe₂ layer, this results in fewer exciton pairs re-combining and a lower enhancement of PL intensity from the 1L MoSe₂ + 1L PEN heterostructure. Moreover, the lower relative QYs of 1L pentacene as compared to WL pentacene (Supplementary Note 4) also contributes to the smaller β value. In 2L pentacene, the charges are extremely mobile and almost follow a band-like mechanism to move within the pentacene layer (Figure 3f).^[14] Hence, the charges will be more diffused along the pentacene layer rather than crossing over the interface of the junction into the MoSe₂ layer. Furthermore, 2L pentacene has the lowest relative QYs among these pentacene films (Supplementary Note 4), in this case, fewer photocarriers transfer to the MoSe₂ and subsequently leads to the small β value and low normalized PL intensity as shown in Figure 3a. In addition, bulk pentacene thin film has the lowest (almost ignorable) PL enhancement factor ($\eta \approx 1.2$, Figure S3) and thus ultralow interlayer charge transfer efficiency, because bulk pentacene layer possesses the band-like charge transport mechanism (similar to 2L pentacene layer) but more traps and disorders in the thin film.^[14] The comparison clearly shows that the efficient exciton pumping is only prominent at the 2D limit.

The strong many-body interactions in monolayer TMDs lead to the formation of robust quasi-particles, such as excitons, trions (charged excitons), and biexciton which are extremely important for the optoelectronics device applications, such as light emitting diodes and optical modulators, *etc.*^[39,39] Besides the efficient interfacial exciton pumping, the hybridization of 2D organic layers in our ultra-thin O-I heterostructures would also allow us to precisely modulate the

many-body interactions in the monolayer TMD *via* engineering the dielectric environment (**Figure 4**).^[32,40] Temperature-dependent (Figure S7) and gate-dependent PL measurements (Figure S8) were conducted to explore the detailed modulation of many-body interactions in our heterostructure systems. In the PL spectra measured from the 1L MoSe₂ sample on SiO₂/Si substrate and in three heterostructures at 83 K, the two PL peaks at ~748 and ~759 nm (Figure 4a) are assigned to be the excitons and trions peaks of 1L MoSe₂, respectively.^[30] Based on the gate-dependent measurements (Figure S8, Supplementary Note 5), those trion peaks as shown in Figure 4a are negatively charged. The binding energy of trion in 1L MoSe₂, energy difference between exciton and trion peak position,^[32,41] was clearly enhanced with the hybridization of organic 2D materials and this enhancement increases with increasing pentacene layer number (Figure 4b). For instance, 1L MoSe₂ on SiO₂/Si sample showed a measured trion binding energy of ~23.4 meV, which matches well with the reported value.^[32,42] The trion binding energy of 1L MoSe₂ on 2L PEN is enhanced by 4.9 meV as compared with that of 1L MoSe₂ on SiO₂/Si (Figure 4b). The PL intensity ratio between trion and exciton peaks was also enhanced with the hybridization of pentacene and this enhancement also increases with increasing pentacene layer number (Figure 4c). It's expected that many-body interactions in low-dimensional materials, such as monolayer TMDs, are sensitive to dielectric environment.^[30] Larger dielectric screening effect can lead to smaller trion binding energy and lower PL intensity ratio between trion and exciton.^[30,43] The dielectric constant of pentacene, h-BN and SiO₂ has the following ranking: h-BN>SiO₂>pentacene.^[43,44] Therefore, the pentacene layer with lower dielectric constant will reduce the total screening effect on the 1L MoSe₂ sitting on top, leading to the enhanced trion binding energy of MoSe₂ in the heterostructures compared with that in the 1L MoSe₂ sample on SiO₂/Si (Figure 4d-f). In addition, the thicker pentacene layer can lead to

the more reduced dielectric screening, thus higher trion binding energy (Figure 4b) and higher ratio of PL intensity between trions and excitons (Figure 4c). The photo-excitation induced charge transfer within the heterostructures, from the small excitation power used, has a negligible effect on the ratio of PL intensity between trions and excitons (Supplementary Note 6). Our results provide a general way to precisely engineer the many-body interactions in atomically thin semiconductors, triggering new applications in ultra-thin spintronic and valleytronic devices.

In conclusion, we have demonstrated an O-I 2D vdW heterojunction comprising of ultrathin organic pentacene and monolayer MoSe₂. Our PL and PLE measurements strongly suggest the type-I band alignments in those heterostructures, which provide a powerful platform to explore the efficient and layer-dependent exciton pumping across the O-I interfaces. The interfacial exciton pumping efficiency could be up to ~86 times higher than the photoexcitation pumping in 1L MoSe₂, considering that the pentacene layer has much lower optical absorption. The high interfacial exciton pumping efficiency is related to ultra-fast energy transfer across the O-I interfaces, the high quantum yields of the organic semiconductors and the relaxation pathways of the photoexcited carriers in the hybrid system. The layer-dependent pumping efficiency is also highly related to the layer-dependent carrier transport in the atomically thin pentacene layers. Moreover, the hybridization of those atomically thin organic 2D materials has significantly modulated the many-body interactions in the monolayer MoSe₂ *via* precise dielectric engineering. Our demonstrations provide a general and new way to manipulate the exciton pumping and to engineer the many-body interactions in atomically thin semiconductors, enabling various novel and exciting optoelectronic implications in lighting, energy harvesting, spintronic and valleytronic devices, *etc.*

EXPERIMENTAL METHODS

This article is protected by copyright. All rights reserved.

Device fabrication and characterization. Ultrathin two-dimensional pentacene single crystal samples were fabricated through the physical vapor deposition method over few-layer h-BN films on a SiO₂/Si substrate (290 nm thermal oxide on p⁺-doped silicon).^[14] The pentacene films were characterized by an optical microscope, AFM and Raman spectroscopy to identify the number of layers and topological information. Pentacene layer-dependent heterostructures were fabricated by dry transfer of 1L MoSe₂ flakes on the designated pentacene samples. For the MOS structure, used for back gate-dependent PL measurements, we transferred the 100 nm thick gold electrode to contact part of the MoSe₂ flakes as the probing pad.

Optical characterization. PL and Raman measurements were conducted using a Horiba LabRAM system equipped with a confocal microscope, a charge-coupled device (CCD) Si detector, and a 532 nm diode-pumped solid-state (DPSS) laser as the excitation source. For temperature-dependent (above 83 K) measurements, the sample was placed into a microscope-compatible chamber with a low-temperature controller (using liquid nitrogen as the coolant). The electrical bias was applied using a Keithley 4200 semiconductor analyzer. The μ -PLE system employed in this study was a Horiba LabRAM system equipped with confocal optics and a charge-coupled-device (CCD) array silicon detector. A supercontinuum excitation light source (NKT SuperK Extreme EXR-20) with a tunable wavelength range between 490 nm and 2000 nm was employed. In this work, excitation wavelengths between 490 nm and 750 nm were used with a bandwidth of 12 nm for the chosen wavelengths, and the on-sample power was kept constant for all excitation wavelengths. The wavelength selection was achieved using a SuperK VARIA attachment allowing the tuning of both the center wavelength and the bandwidth of the filtered light. The laser light was focused on the sample surface *via* an objective lens. The diameter of the illuminated spot on the samples is $\sim 2 \mu\text{m}$. The

spectral response of the entire system was determined with a calibrated halogen-tungsten light source. Time-resolved PL (TRPL) measurements were conducted in a setup that incorporates micro PL spectroscopy with a time-correlated single-photon counting (TCSPC) system. A linearly polarized pulsed laser (frequency doubled to 522 nm, with a 300 fs pulse width and a 20.8 MHz repetition rate) was directed to a high numerical aperture (NA = 0.7) objective (Nikon S Plan 60×). The PL signal was collected by a grating spectrometer, thereby either recording the PL spectrum through the CCD (Princeton Instruments, PIXIS) or detecting the PL intensity decay by a Si single-photon avalanche diode and the TCSPC (PicoHarp 300) system with a resolution of 20 ps. All the PL spectra were corrected for the instrument response. All the optical path length (OPL) characterizations were obtained using a phase-shifting interferometer (Veeco NT9100).

Competing financial interests

The authors declare that they have no competing financial interests.

Supporting Information

Supporting information is available from the Wiley Online Library or from the author.

Acknowledgments

Funding: We would like to acknowledge the facility support from Professor Chennupati Jagdish's group at the ANU, ACT node of the Australian National Fabrication Facility (ANFF). We also acknowledge financial support from ANU Ph.D. student scholarship, China Scholarship Council, ANU Major Equipment Committee fund (No. 14MEC34), Australian Research Council (ARC) Discovery Early Career Researcher Award (DECRA) DE140100805. **Author Contributions:** L.L.Z and A.S. contributed

This article is protected by copyright. All rights reserved.

equally to this work. Y.R.L. and X.R.W. conceived and supervised the project; L.L.Z., Y.H.Z, Y.J.C., B. L, X. S. and A.K. prepared the samples; H. N. and D. M. contributed to the PLE set up; L.L.Z. and B.W.W conducted the measurements; L.L.Z. did the PSI measurements. L.L.Z., A.S. and Y.Z. did the PL measurements; B.W.W., M.H.D., B.W., H.N., D.M., Z.Y.L. and Y.S. contributed to data analysis; Z.W and Z.F.Y did the absorption simulation; Y.R.L, L.L.Z. and A.S. cowrote the paper; all authors discussed the results and commented on the manuscript.

Reference

- [1] Lee, G.-H., Lee, C.-H., van der Zande, A. M., Han, M., Cui, X., Arefe, G., Nuckolls, C., Heinz, T. F., Hone, J. & Kim, P., *APL Mater.* **2014**, *2*, 092511.
- [2] Lin, Y. C., Ghosh, R. K., Addou, R., Lu, N., Eichfeld, S. M., Zhu, H., Li, M. Y., Peng, X., Kim, M. J., Li, L. J., Wallace, R. M., Datta, S. & Robinson, J. A., *Nat. Commun.* **2015**, *6*, 7311.
- [3] Lee, C.-H., Lee, G.-H., van der Zande, A. M., Chen, W., Li, Y., Han, M., Cui, X., Arefe, G., Nuckolls, C., Heinz, T. F., Guo, J., Hone, J. & Kim, P., *Nat. Nanotechnol.* **2014**, *9*, 676-681.
- [4] Wang, Q. H., Kalantar-Zadeh, K., Kis, A., Coleman, J. N. & Strano, M. S., *Nat. Nanotechnol.* **2012**, *7*, 699-712.
- [5] Jariwala, D., Howell, S. L., Chen, K. S., Kang, J., Sangwan, V. K., Filippone, S. A., Turrisi, R., Marks, T. J., Lauhon, L. J. & Hersam, M. C., *Nano Lett.* **2016**, *16*, 497-503.
- [6] Bettis Homan, S., Sangwan, V. K., Balla, I., Bergeron, H., Weiss, E. A. & Hersam, M. C., *Nano Lett.* **2016**.
- [7] Cho, E. H., Song, W. G., Park, C. J., Kim, J., Kim, S. & Joo, J., *Nano Res.* **2014**, *8*, 790-800.
- [8] Jariwala, D., Marks, T. J. & Hersam, M. C., *Nat. Mater.* **2017**, *16*, 170-181.
- [9] Zhu, T., Yuan, L., Zhao, Y., Zhou, M. W., Wan, Y., Mei, J. G. & Huang, L. B., *Sci. Adv.* **2018**, *4*, 8.
- [10] Liu, X., Gu, J., Ding, K., Fan, D., Hu, X., Tseng, Y. W., Lee, Y. H., Menon, V. & Forrest, S. R., *Nano Lett.* **2017**, *17*, 3176-3181.
- [11] Zhang, F., Ma, Y., Chi, Y., Yu, H., Li, Y., Jiang, T., Wei, X. & Shi, J., *Sci. Rep.* **2018**, *8*, 8208.
- [12] Ozaki, H., *J. Chem. Phys.* **2000**, *113*, 6361-6375.
- [13] Menozzi, C., Corradini, V., Cavallini, M., Biscarini, F., Betti, M. G. & Mariani, C., *Thin Solid Films* **2003**, *428*, 227-231.

- [14] Zhang, Y., Qiao, J., Gao, S., Hu, F., He, D., Wu, B., Yang, Z., Xu, B., Li, Y., Shi, Y., Ji, W., Wang, P., Wang, X., Xiao, M., Xu, H., Xu, J. B. & Wang, X., *Phys. Rev. Lett.* **2016**, *116*, 016602.
- [15] He, D., Zhang, Y., Wu, Q., Xu, R., Nan, H., Liu, J., Yao, J., Wang, Z., Yuan, S., Li, Y., Shi, Y., Wang, J., Ni, Z., He, L., Miao, F., Song, F., Xu, H., Watanabe, K., Taniguchi, T., Xu, J. B. & Wang, X., *Nat. Commun.* **2014**, *5*, 5162.
- [16] Hill, I. G., Kahn, A., Soos, Z. G. & R.A. Pascal, J., *Chem. Phys. Lett.* **2000**, *327*, 8.
- [17] Nakamura, S., Senoh, Masayuki, Iwasa, Naruhito & Nagahama, Shin-ichi, *Jpn. J. Appl. Phys.* **1995**, *34*, 3.
- [18] Hui, C., Jun, K., Hasan, S., Bin, C., Aslihan, S., Kedi, W., Francois, P., Xiuqing, M. & Sefaattin, T., *Nanotechnology* **2016**, *27*, 065203.
- [19] Bellus, M. Z., Li, M., Lane, S. D., Ceballos, F., Cui, Q., Zeng, X. C. & Zhao, H., *Nanoscale Horiz.* **2017**, *2*, 31-36.
- [20] Kang, S. J., Lee, G.-H., Yu, Y.-J., Zhao, Y., Kim, B., Watanabe, K., Taniguchi, T., Hone, J., Kim, P. & Nuckolls, C., *Adv. Funct. Mater.* **2014**, *24*, 5157-5163.
- [21] Lee, G. H., Yu, Y. J., Cui, X., Petrone, N., Lee, C. H., Choi, M. S., Lee, D. Y., Lee, C. G., Yoo, W. J., Watanabe, K. J., Taniguchi, T., Nuckolls, C., Kim, P. & Hone, J., *Acs Nano* **2013**, *7*, 6.
- [22] Florian, M., Hartmann, M., Steinhoff, A., Klein, J., Holleitner, A. W., Finley, J. J., Wehling, T. O., Kaniber, M. & Gies, C., *Nano Lett.* **2018**, *18*, 2725-2732.
- [23] Castellanos-Gomez, A., Buscema, M., Molenaar, R., Singh, V., Janssen, L., van der Zant, H. S. J. & Steele, G. A., *2D Mater.* **2014**, *1*, 011002.
- [24] Gong, Y., Lin, J., Wang, X., Shi, G., Lei, S., Lin, Z., Zou, X., Ye, G., Vajtai, R., Yakobson, B. I., Terrones, H., Terrones, M., Tay, B. K., Lou, J., Pantelides, S. T., Liu, Z., Zhou, W. & Ajayan, P. M., *Nat. Mater.* **2014**, *13*, 1135-1142.
- [25] Hong, X., Kim, J., Shi, S. F., Zhang, Y., Jin, C., Sun, Y., Tongay, S., Wu, J., Zhang, Y. & Wang, F., *Nat. Nanotechnol.* **2014**, *9*, 682-686.
- [26] Özcelik, V. O., Azadani, J. G., Yang, C., Koester, S. J. & Low, T., *Phys. Rev. B* **2016**, *94*, 035125.
- [27] Gong, C., Zhang, H., Wang, W., Colombo, L., Wallace, R. M. & Cho, K., *Appl. Phys. Lett.* **2013**, *103*, 053513.
- [28] Yoshida, H., Yamada, K., Tsutsumi, J. y. & Sato, N., *Phys. Rev. B* **2015**, *92*.
- [29] Shionoiri, M., Kozasa, M., Kera, S., Okudaira, K. K. & Ueno, N., *Jpn. J. Appl. Phys.* **2007**, *46*, 1625-1629.
- [30] Pei, J., Yang, J., Wang, X., Wang, F., Mokkapatil, S., Lu, T., Zheng, J. C., Qin, Q., Neshev, D., Tan, H. H., Jagadish, C. & Lu, Y., *Acs Nano* **2017**.
- [31] Tonndorf, P., Schmidt, R., Böttger, P., Zhang, X., Börner, J., Liebig, A., Albrecht, M., Kloc, C., Gordan, O., Zahn, D. R. T., Vasconcellos, S. M. & Bratschitsch, R., *Opt. Express* **2013**, *21*, 9.
- [32] Ross, J. S., Wu, S., Yu, H., Ghimire, N. J., Jones, A. M., Aivazian, G., Yan, J., Mandrus, D. G., Xiao, D., Yao, W. & Xu, X., *Nat. Commun.* **2013**, *4*, 1474.
- [33] Rao, A., Wilson, M. W. B., Albert-Seifried, S., Di Pietro, R. & Friend, R. H., *Phys. Rev. B* **2011**, *84*.

- [34] Amani, M., Lien, D. H., Kiriya, D., Xiao, J., Azcatl, A., Noh, J., Madhvapathy, S. R., Addou, R., KC, S., Dubey, M., Cho, K., Wallace, R. M., Lee, S., He, J., Ager III, J. W., Zhang, X. & Ali Javey, E. Y., *Science* **2015**, *350*, 4.
- [35] Palummo, M., Bernardi, M. & Grossman, J. C., *Nano Lett.* **2015**, *15*, 2794-2800.
- [36] Kozawa, D., Kumar, R., Carvalho, A., Kumar Amara, K., Zhao, W., Wang, S., Toh, M., Ribeiro, R. M., Castro Neto, A. H., Matsuda, K. & Eda, G., *Nat. Commun.* **2014**, *5*, 4543.
- [37] Tabachnyk, M., Ehrler, B., Gelinias, S., Bohm, M. L., Walker, B. J., Musselman, K. P., Greenham, N. C., Friend, R. H. & Rao, A., *Nat. Mater.* **2014**, *13*, 1033-1038.
- [38] Akshay Rao, Mark W. B. Wilson, Justin M. Hodgkiss, Sebastian Albert-Seifried, Heinz Baessler & Friend, R. H., *J. Am. Chem. Soc.* **2010**, *132*, 6.
- [39] Sharma, A., Yan, H., Zhang, L., Sun, X., Liu, B. & Lu, Y., *Acc. Chem. Res.* **2018**.
- [40] Ugeda, M. M., Bradley, A. J., Shi, S. F., da Jornada, F. H., Zhang, Y., Qiu, D. Y., Ruan, W., Mo, S. K., Hussain, Z., Shen, Z. X., Wang, F., Louie, S. G. & Crommie, M. F., *Nat. Mater.* **2014**, *13*, 1091-1095.
- [41] Jiong Yang, Tiejun Lu, Ye Win Myint, Jiajie Pei, Daniel Macdonald, Jin-Cheng Zheng & Lu, Y., *Acs Nano* **2015**, *9*, 7.
- [42] Kylänpää, I. & Komsa, H.-P., *Phys. Rev. B* **2015**, *92*.
- [43] Lin, Y., Ling, X., Yu, L., Huang, S., Hsu, A. L., Lee, Y. H., Kong, J., Dresselhaus, M. S. & Palacios, T., *Nano Lett.* **2014**, *14*, 5569-5576.
- [44] Kim, C. H., Yaghmazadeh, O., Tondelier, D., Jeong, Y. B., Bonnassieux, Y. & Horowitz, G., *J. Appl. Phys.* **2011**, *109*, 083710.

Figure Captions

Figure 1 | Characterization of layer-dependent heterostructures comprising of monolayer MoSe₂ and 2D pentacene. **a**, Schematic diagram of heterostructure of monolayer MoSe₂ on 2D pentacene. **b**, Optical image before heterostructure formation showing wetting layer (WL), one-layer (1L), and two-layer (2L) pentacene regions. Scale bar, 10 μm. **c**, Optical image after 1L MoSe₂ transferred on pentacene. Scale bar, 10 μm. (I) Heterostructure of 1L MoSe₂ on WL Pentacene (1L MoSe₂ + WL PEN). (II) Heterostructure of 1L MoSe₂ on 1L Pentacene (1L MoSe₂ + 1L PEN). (III) Heterostructure of 1L MoSe₂ on 2L Pentacene (1L MoSe₂ + 2L PEN). Scale bar, 10 μm. **d**, AFM image of the dotted rectangular area shown in **b**. Inset: height measurements along the dashed line showing atomic layer

This article is protected by copyright. All rights reserved.

thickness. **e**, (I) PL spectra of 1L MoSe₂ + WL PEN heterostructure, 1L MoSe₂ and WL PEN. (II) PL spectra from 1L MoSe₂ + 1L PEN heterostructure, 1L MoSe₂ and 1L PEN. (III) PL spectra from 1L MoSe₂ + 2L PEN heterostructure, 1L MoSe₂ and 2L PEN.

Figure 2 | Confirmation of type-I band alignment by photoluminescence excitation (PLE). **a**, Band alignment diagram of a MoSe₂/Pentacene heterostructure, which forms a type I heterostructure. **b-c**, Measured PL spectra of 1L MoSe₂ from SiO₂/Si substrate and from 1L MoSe₂ + WL PEN heterostructure, with different excitation wavelengths, 532 nm (b) and 750 nm (c). **d**, Measured PL enhancement factor η from 1L MoSe₂ + WL PEN heterostructure as a function of excitation wavelength. The enhancement factor η is defined as the intensity ratio of PL peak at ~788 nm between a heterostructure (HS) and the monolayer MoSe₂ on SiO₂/Si substrate.

Figure 3 | Efficient and layer-dependent interfacial exciton pumping. **a**, Exciton pumping efficiency enhancement factor β (Left), normalized PL intensity (by pentacene layer thickness) of various kinds of heterostructures as compared with 1L MoSe₂ (Right). **b**, Schematic of the exciton relaxation channels in the MoSe₂/pentacene heterostructure for excitation at S state resonance. GS represents ground state and S represents the excitation state. The wavy red (K_r) and straight black arrows (K_{nr}) represent radiative and nonradiative decay process, respectively. K is associated with each transition including in intravalley thermalization or intervalley scattering. **c**, Measured time-resolved PL traces at room temperature for exciton peak ~788 nm from oxide-supported monolayer MoSe₂ and for peak ~590 nm from WL pentacene samples, IR represents instruments response curve. Based on the deconvolution with respect to the instrument response, double exponential equation $I = A \exp\left(-\frac{t}{\tau_1}\right) + B \exp\left(-\frac{t}{\tau_2}\right) + C$ was used for the fitting. For 1L MoSe₂, τ_1 and τ_2 were extracted to be 36 and 448 ps, respectively, which are considered to be non-radiative and radiative lifetimes, respectively.^[30,34,35] For WL pentacene, the single exponential equation $I = A \exp\left(-\frac{t}{\tau}\right) + C$, τ was extracted to be 1128 ps. **d**, Schematic diagram shows the charge transfer between WL PEN (bottom) and 1L MoSe₂ (top). The dotted ellipse shows long-range intra-layer coulombic coupling within WL PEN. **e**, Schematic diagram shows the charge transfer 1L PEN (bottom) and 1L MoSe₂ (top). The horizontal crooked arrows show the hopping mechanism of charge transfer within 1L PEN. **f**,

This article is protected by copyright. All rights reserved.

Schematic diagram shows the charge transfer between 2L PEN (bottom) and 1L MoSe₂ (top). The horizontal arrows show the band-like mechanism of charge transfer within 2L PEN.

Figure 4 | Layer-dependent modulation of the trion binding energy in 1L MoSe₂ via dielectric engineering. **a**, Measured PL spectra of 1L MoSe₂ from SiO₂/Si substrate, 1L MoSe₂ + WL PEN, 1L MoSe₂ + 1L PEN and 1L MoSe₂ + 2L PEN heterostructures at 83 K. The PL spectrum was fitted by Lorentz function (Black scatter lines are experimental data, red lines are labeled as Exciton Peak, blue lines are labeled as Trion Peak, and olive lines are the cumulative fitting results). **b**, Measured trion binding energy (energy difference between exciton and trion peaks) of 1L MoSe₂ from SiO₂/Si substrate, 1L MoSe₂ + WL PEN, 1L MoSe₂ + 1L PEN and 1L MoSe₂ + 2L PEN heterostructures at 83 K. **c**, Measured trion/exciton PL peak intensity ratio of 1L MoSe₂ from SiO₂/Si substrate, 1L MoSe₂ + WL PEN, 1L MoSe₂ + 1L PEN and 1L MoSe₂ + 2L PEN heterostructures at 83 K. **d-f**, Schematic representation of negatively charged trions in 1L MoSe₂ over different substrates: SiO₂ (d), WL PEN (e) and 2L PEN (f). Pentacene has lower dielectric constant than SiO₂ and h-BN. The PEN layer serves as a low-dielectric spacing layer, which provides reduced dielectric screening and leads to enhanced trion binding energy (smaller trion size) in 1L MoSe₂.

Author Manuscript

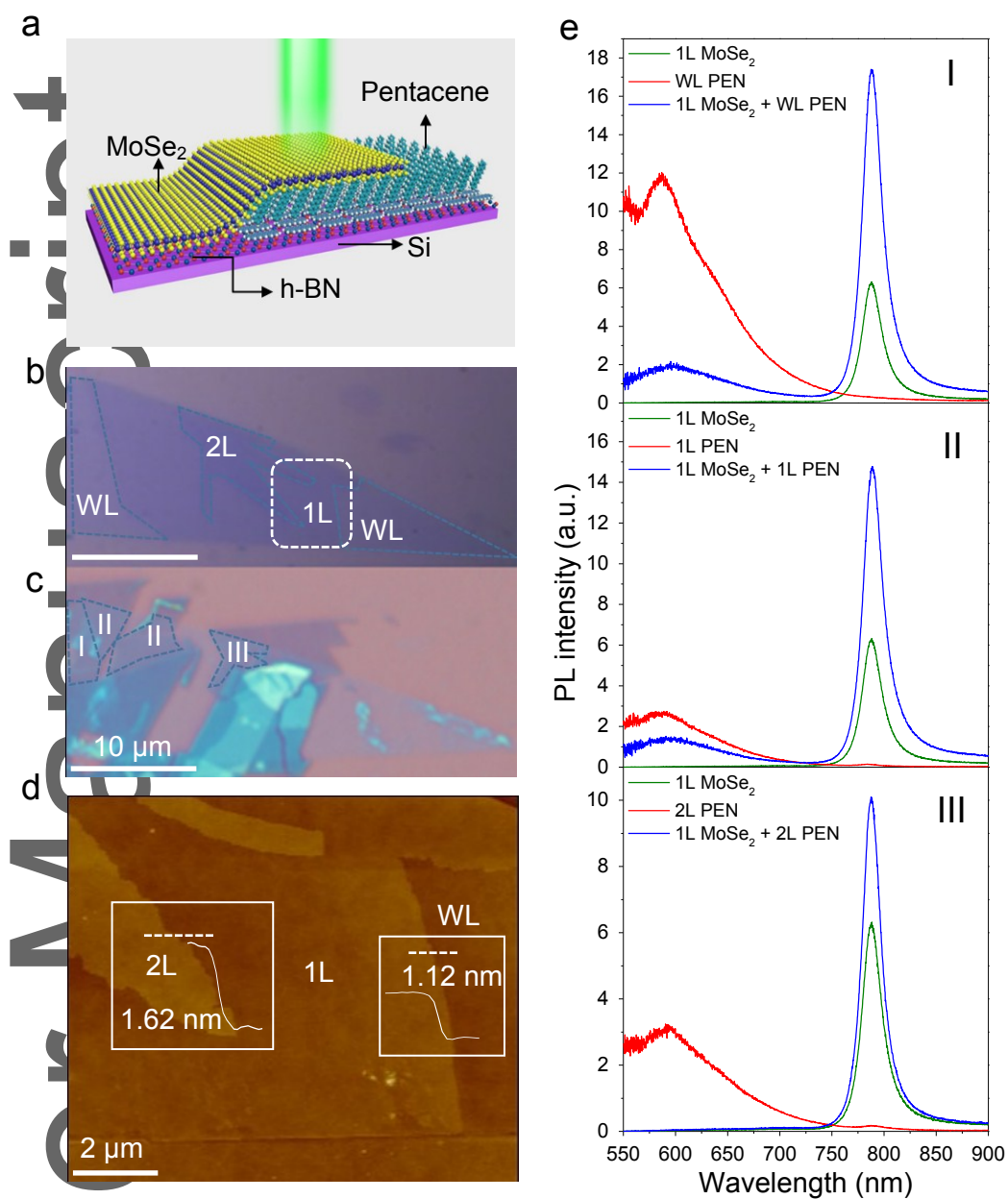


Figure 1

This article is protected by copyright. All rights reserved.

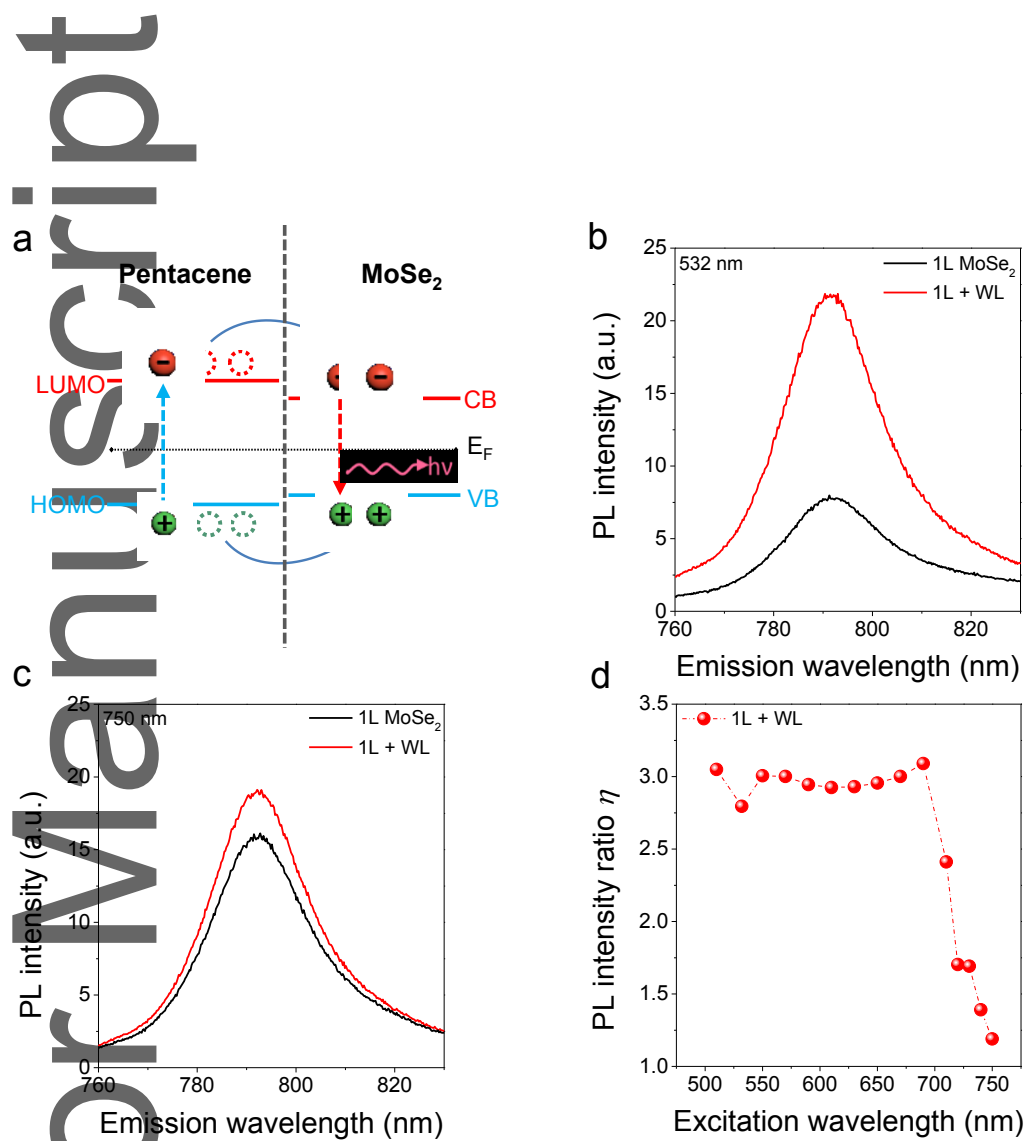


Figure 2

This article is protected by copyright. All rights reserved.

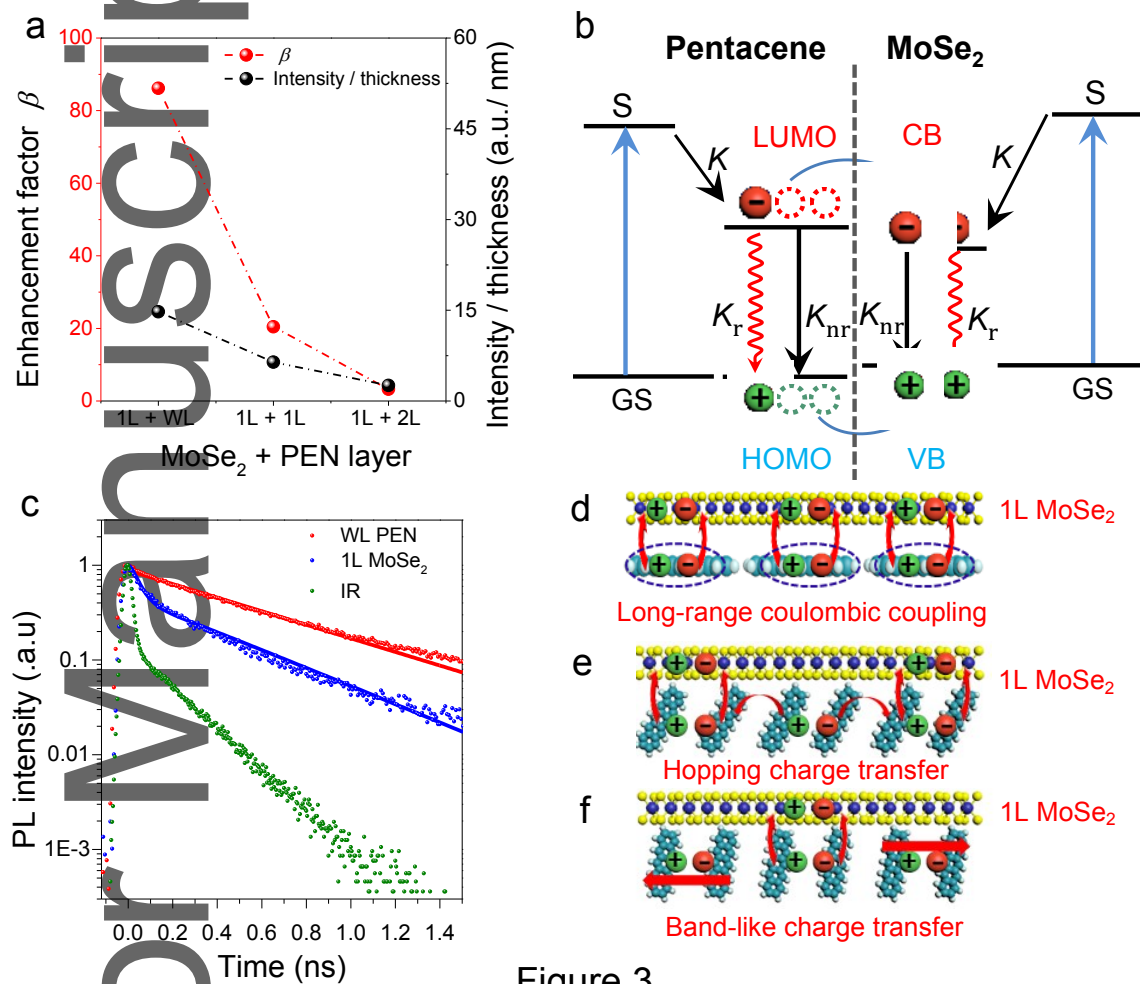


Figure 3

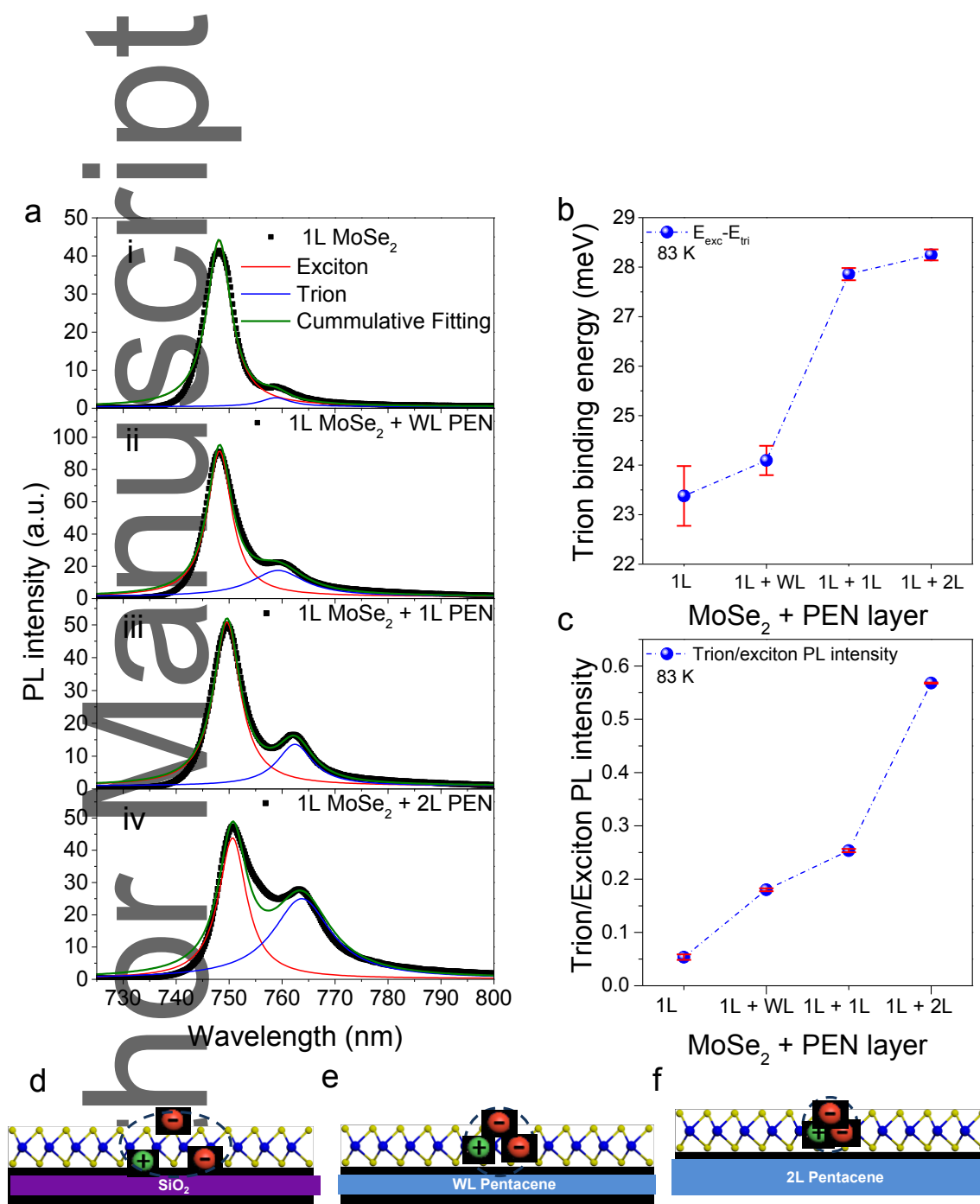


Figure 4

This article is protected by copyright. All rights reserved.

Atomically thin and layer-dependent (organic-inorganic) O-I heterostructures are fabricated, which comprise monolayer MoSe₂ and two-dimensional limit (2D) pentacene. The heterostructures are observed to be type I band alignment, showing efficient and layer-dependent exciton pumping. In addition, substrate-related and pentacene layer-dependent modulation of the trion binding energies in monolayer TMDCs is also demonstrated.

