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Amplification of interlayer exciton emission in twisted $\text{WSe}_2/\text{WSe}_2/\text{MoSe}_2$ heterotrilayers



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Van der Waals heterostructures based on transition metal dichalcogenides exhibit physical properties that depend on their monolayer constituents' twisting angle and stacking order. Particularly in type-II heterostructures, low-energy photoluminescence is dominated by interlayer excitons, resulting in low emission yields, which drastically hampers their optoelectronic applicability. This study reports on the photoluminescence quantum yield of heterostructures consisting of $\text{WSe}_2/\text{WSe}_2/\text{MoSe}_2$ twisted layers. Our findings show that the additional WSe_2 monolayer in the trilayer system enhances the low-energy photoluminescence by more than an order of magnitude depending on the $\text{WSe}_2/\text{WSe}_2$ twist-angle in comparison to their $\text{WSe}_2/\text{MoSe}_2$ heterobilayer counterpart. Furthermore, combining density functional theory calculations and extracted degree of circular polarization, we identify excitonic signatures arising from hybridized states that originate from the additional WSe_2 layer. In addition to providing an additional understanding of hybridization effects in 2D semiconducting heterostructures, our findings provide a viable method to enhance emission in van der Waals heterostructures, relevant for studying the fundamental properties of excitons and enabling optoelectronic applications with high luminescence yield.

Interlayer excitons in heterostructures of transition metal dichalcogenides (TMDCs) have recently been identified as a class of strongly bound quasiparticles^{1–6}. These emerging materials are of great interest for both fundamental physics and practical applications, as they facilitate the investigation of intriguing optoelectronic properties and the development of innovative nanophotonic devices. A distinctive aspect of these TMDC heterostructures is that their electronic and optical properties can be controlled by conveniently changing the twist angle at which the layers are stacked. The twist angle determines the periodicity and confinement potential of the moiré superlattice, subsequently impacting the exciton physics of TMDC heterostructures⁷. Therefore, remarkable many-body phenomena, including exciton interactions, band gap renormalization, and Mott transition, have emerged in these systems^{4,8,9}. In addition, the moiré pattern associated with the atomic reconstruction^{10–14} has a significant impact on the electronic band structure, which results in the formation of flat minibands^{2,5} and hybridized excitonic states², both of which are often observed in heterostructures composed of TMDCs.

Among the various 2D semiconducting twisted bilayers presented in the literature, the $\text{WSe}_2/\text{MoSe}_2$ heterostructure exhibits a lattice mismatch of approximately 0.1%, resulting in a moiré length of dozens of nanometers^{6,15}. It also features a type-II band alignment that accommodates interlayer exciton (iX) with emission below 1.4 eV at cryogenic temperatures, when electrons and holes bound by Coulomb forces occupying the conduction band (CB) and valence band (VB) at the K valleys, respectively, in separate monolayers^{1,12,15–19}. These characteristics can together form trapping sites that behave as twist-angle-controlled quantum-dot-like confinement potentials for excitons⁷.

Despite the ultrafast transfer of interlayer charges between the CB and VB of the corresponding MoSe_2 and WSe_2 ^{16,20}, both intralayer photoluminescence (PL) intensity for the monolayers (ML) and the interlayer excitonic emission for the heterostructures exhibits a notable low PL yield, which proves to be a significant bottleneck for optoelectronic applications. The low luminescence output of these heterostructures can be attributed to various factors, such as the non-direct alignment of bands at the K point of the Brillouin zone, the dependence of layer separation on the twist angle, as

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well as the spatial separation of electron and hole wave functions, which leads to lessened coupling strength¹⁷. Therefore, it is essential to investigate TMDC heterostructures that display exceptional optical features in combination with powerful PL emission.

In this work, we study artificially stacked heterobilayers (HBL) and heterotrilayers (HTL) based on WSe₂ and MoSe₂ twisted MLs. Prior research on HTL systems includes either MLs stacked with other natural bilayers^{21,22} or HTL systems in a sandwich-like configuration (ML₁/ML₂/ML₁) with arbitrary twist angles^{23–25}. Importantly, the influence of the twist angle on the optical characteristics of the HTL system remains unclear and poorly explored. In sharp contrast to previous research, we are investigating WSe₂/WSe₂/MoSe₂ HTL systems in which all MLs are mechanically stacked and twisted.

In our nanofabrication procedure, we stacked each layer separately, controlling the twist angle between all constituent MLs. The stacking arrangement for our hole transport HTL system consists of ML ²WSe₂/ML ¹WSe₂/ML MoSe₂ covered by a thin (<8 nm) layer of hBN, working as a passivating and protective layer (Fig. 1a). We considered two samples, HS1 and HS2, with twist angles between the individual WSe₂ MLs (θ_{Bi}) of 0° and 57°, respectively. The 2H stacked configuration for the twisted heterobilayer closely resembles the twist angle found in the WSe₂/MoSe₂ heterostructure (θ_{HS}), which is 44° and 58°, respectively. The twist angles were determined by polarization-resolved second harmonic generation (SHG) measurements²⁶. Additional details can be found in the methods section and Supplementary Note 1. The HBL and HTL regions are labelled as HBL1

(HBL2) and HTL1 (HTL2) for samples HS1 (HS2), respectively. Figure 1a displays the stacked arrangement of our artificially twisted heterostructure made of ²WSe₂/¹WSe₂/MoSe₂. Figure 1b shows the HTL and HBL areas are made up of ²WSe₂/¹WSe₂/MoSe₂ and ¹WSe₂/MoSe₂, respectively, along with (θ_{Bi}) and (θ_{HS}).

Upon comparing the HBL and HTL regions of samples HS1 and HS2 using micro-photoluminescence (μ PL), reflectance contrast, photoluminescence excitation (PLE), and degree of circular polarization (DCP) measurements, we observed a significant difference in optical response at cryogenic temperatures. Notably, the HTL system showed a considerable enhancement in emission, nearly 20 times, compared to its HBL region for HS1. Further, we use density functional theory (DFT) to compute the electronic band structures of our twisted HBL and HTL systems. The calculated dipole matrix elements between VB and CB states give insight into direct transitions in twisted heterostructure systems. Our findings showcase diverse opportunities that arise from manipulating the properties of TMDC heterostructures through twist-angle engineering. In this study, we present an efficient method for manipulating the number of monolayers to regulate the interlayer excitonic response and PL yield in twisted heterostructures. Our investigation of heterotrilayers extends beyond simple heterobilayers and creates various avenues for exploring the parameter space of TMDC quantum materials. This includes analyzing the stacking order and twist angles between all constituent layers, thereby offering exciting prospects for further research and potential applications.

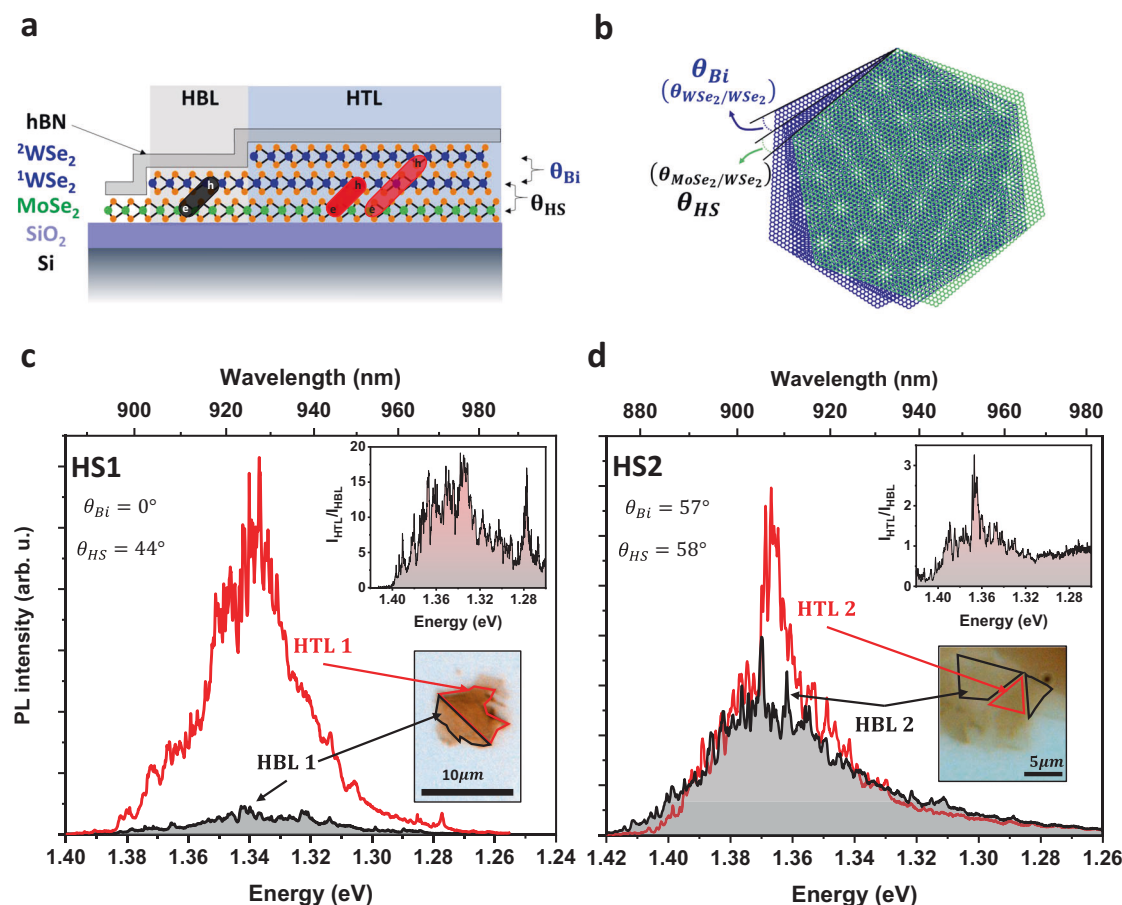


Fig. 1 | Twisted ²WSe₂/¹WSe₂/MoSe₂ heterotrilayers. **a** Schematic representation of the HTL system showcasing the stacking order and the substrate configuration along with potential interlayer and momentum-indirect exciton formation between the layers. **b** A simplified illustration of the HTL system (WSe₂ and MoSe₂ are shown in blue and green, respectively) showcasing complex moiré superlattices with the twist angle (θ_{Bi} and θ_{HS}) between the layers. Photoluminescence spectra for **c** HS1 and **d** HS2 measured at 4 K. The PL emission from the HTL (HBL) region is plotted

in red (black) lines. The optical microscope images highlight the HBL and HTL regions with black and red outlines, respectively. The twist angle for the MoSe₂/WSe₂ heterostructure (θ_{HS}) in HS1 (HS2) is 44° (58°) and the twist angle for stacked WSe₂ MLs (θ_{Bi}) is close to 0° (57°). The inset in **c**, **d** shows the ratio of measured intensity from HTL and HBL regions (I_{HTL}/I_{HBL}) of both samples, demonstrating an enhancement factor of nearly 20 and ~3 for HS1 and HS2, respectively.

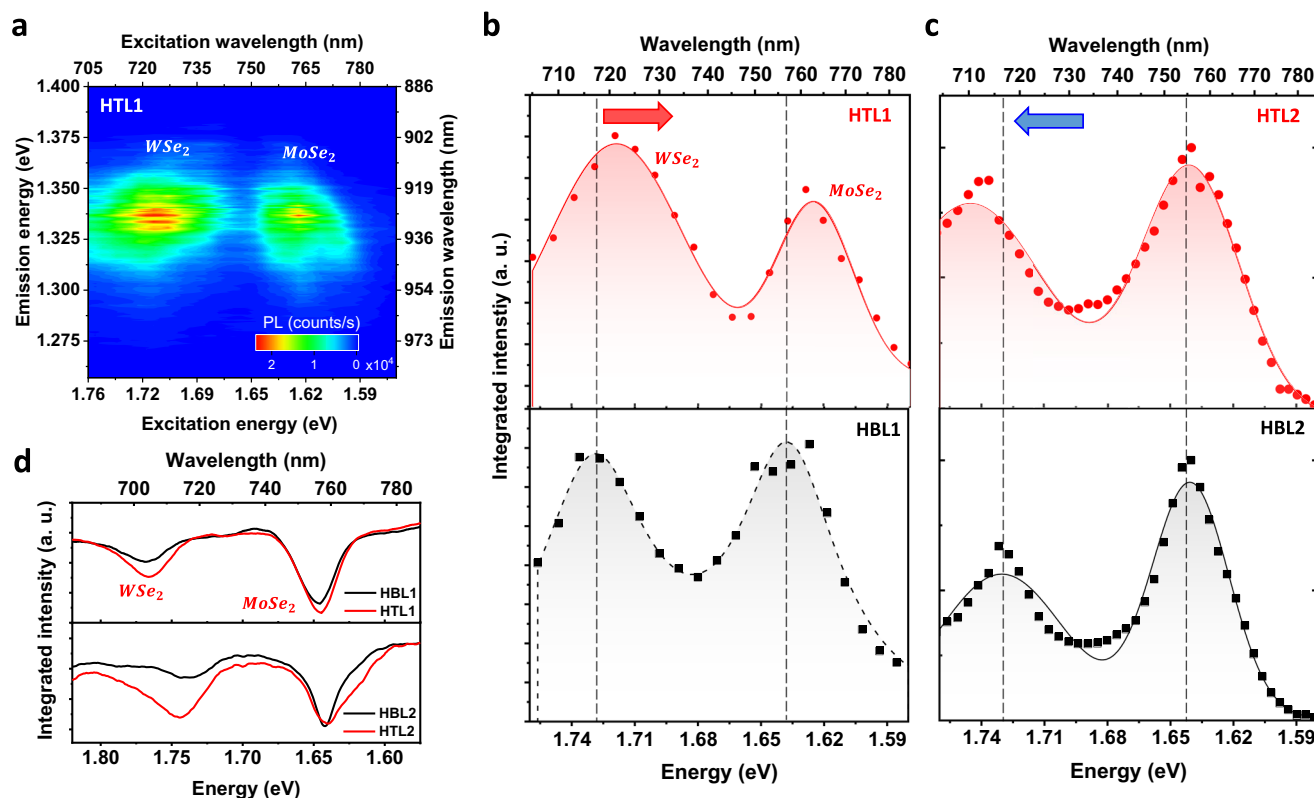


Fig. 2 | Photoluminescence excitation spectroscopy of twisted heterobilayers and heterotrilayers. **a** False color PLE map of emission from the HTL1 region manifesting the intralayer exciton resonances of WSe₂ and MoSe₂. **b, c** Direct comparison between the PLE resonances recorded from all four studied regions of the two samples (HS1, HS2). The integrated intensity as a function of excitation energy is plotted in (**b, c**), upper panel, for HTL (red dots) and lower panel for HBL (black dots). Further, the PLE response is fitted with a double Gaussian function (solid line

with shaded area), see Table HS1 for fit parameters. The vertical dashed black line helps to identify energy shifts (red and blue arrow) of PLE resonances. **d** Reflectance contrast measurements on the HS1 and HS2 with all considered regions (black curve for HBL, red curve for HTL). In the HTL regions, the light absorption is stronger than in HBL regions, particularly from the A exciton of WSe₂ due to the additional WSe₂ ML. The energy shift of WSe₂ absorption in HTL1 and HTL2 region is attributed to twist angle induced hybridization of intralayer exciton states²⁹.

Results

Amplification of photoluminescence

To investigate the optical emission around the iX energy in the HBL and HTL of samples HS1 and HS2, we utilized PL spectroscopy at 4 K with resonant excitation at the WSe₂ intralayer transition around 1.72 eV (additional details in Methods section). Figure 1c, d displays the characteristic PL emission from iX in ¹WSe₂/MoSe₂ HBLs, ranging from 1.3 to 1.4 eV^{1,3,12,16–18}. The greater physical separation between interlayers due to the large twist angle leads to significantly lower PL emission intensity of iX from the HBL1 (HS1) region, as opposed to HBL2 (HS2). The separation between layers, which is dependent on the twist angle, reduces the charge transfer. As a result, the population of iX in HBL1 decreases. Our DFT calculations (see Methods section) establish that the oscillator strength of interlayer excitons diminishes as the twist angle increases, consistent with the reduction of the observed emission.

The red curve in the HTL1 region of HS1 shows a significant increase in PL intensity when compared to the black curve in the HBL1 region, as seen in Fig. 1c. In Fig. 1d, we see the PL response of HS2, which has some improvement in the emission intensity of the HTL2 region, but not as noticeable as in HS1. The HTL/HBL ratio of the emission intensity, shown in the inset of Fig. 1c, d, displays a nearly 20-fold increase for HS1 and approximately a 3-fold increase for HS2 at distinct emission energies. We also gathered numerous PL spectra from various points in HS1 and HS2, revealing a significant increase in PL output that remained consistent for the HTL area. This can be seen in Supplementary Note 2. After studying the emissions from both samples (see Fig. 1c, d) and considering how the different layers are arranged, we suggest that the extra layer, purposely twisted at angles around 0° or 60°, creates more pathways for light emission

during the transfer of energy between MoSe₂ ↔ WSe₂ layers. On the other hand, the emission intensity of HTL1 is still less than that of HTL2, specifically due to the large momentum mismatch corresponding to the large twist angle between the ¹WSe₂/MoSe₂ interface.

Influence of the twist angle on the interlayer exciton emission in heterotrilayers

PLE measurements were carried out to study the absorption response of HTLs depending on the twist angle of stacked layers, in which the contribution from the WSe₂ and MoSe₂, separately, can be extracted. A false-colour PLE map that shows the emission intensity based on excitation wavelength (energy) at the HTL1 region (Fig. 2a). By using a pulsed-laser to excite the samples from 1.75 eV (705 nm) to 1.55 eV (790 nm) at constant power, we were able to detect two separate PLE resonances which corresponded to the exciton A of both WSe₂ and MoSe₂ (Fig. 2a). See Methods section, for additional information.

For comparison, PLE data were collected from HBL and HTL regions of HS1 and HS2. The raw results are shown in the Supplementary Note 3. Next, we extracted the integrated intensity for the HTL (HBL) region as a function of energy from the measured PLE, plotted in a color map, which is presented in Fig. 2b, c for both samples. Additionally, we used a Gaussian function to fit the integrated intensity, with fitting parameters presented in Supplementary Table 1. The PLE scan reveals two resonances that match the intralayer exciton (WSe₂ and MoSe₂) of the constituent MLs, displaying a higher response in integrated intensity. It indicates not only an efficient absorption from each ML individually and improved gain from heterostructure but also effective interlayer electron–hole tunneling between WSe₂/MoSe₂ HBL interface, which substantiates the interlayer PL emission in Fig. 1b, c.

The total absorption from MLs in the heterostructure system may not entirely contribute to the iX emission, because of other relaxation channels, such as intralayer excitons and non-radiative decay processes. Therefore, PLE measurements are specifically important to extract the direct contribution of each material to the collected emission (shown in Fig. 1). Based on our analysis (see Supplementary Table 1), we found that in the HBL1 region, the combined integrated intensities of WSe₂ and MoSe₂ are approximately equal, thus indicating similar contributions from both materials. In contrast, in the HTL1 region, the PLE intensity from the HTL area shows that the WSe₂ resonance is enhanced roughly by 2 times compared to the HBL1 area. Meanwhile, the PLE resonance intensity of MoSe₂ does not significantly change in both HTL and HBL for HS1. A similar change in the integrated intensity aspect ratio of WSe₂ is observed for the HBL2 and HTL2 areas (see Fig. 2c and Supplementary Table 1). Furthermore, the weight of each material's absolute PLE may differ from sample to sample, as indicated in the PLE literature^{27,28}. Our PLE findings suggest that the extra WSe₂ ML boosts light absorption and exciton population, leading to the enhanced emission demonstrated in the PL spectra in Fig. 1c, d.

Interestingly, a clear redshift was recorded for the WSe₂ PLE resonance in the HTL1 region in comparison to the HBL1 region (see Fig. 2b), whereas in HS2, WSe₂ PLE resonance shows significant blueshift under the same comparison (Fig. 2c). PLE results underline our assumption that the WSe₂ twisted angle of the top layer plays a crucial role in the band structure of the HTL samples. The strongly enhanced PL yield corresponds to the R-type stacking of the WSe₂ homobilayer, whereas the H-type stacking configuration only moderately alters the emission response. To explain our findings, we discuss the hybridization phenomenon in twisted bilayers, responsible for altering the band structure of stacked TMDC system^{29,30}. Previously, Merkl et al.²⁹ and Lin et al.³⁰ investigated the angle dependence of intra- and interlayer excitons in WSe₂ homobilayers, where intra- and interlayer hybridization directly affects the transitions in momentum space. As a result, the twist angle-dependent energy shifts, such as a blueshift for WSe₂ with 2H stacking and redshift with R stacking, are observed. Additionally, due to the spin-orbit splitting and opposite spin orientation of valleys, the hybridization of states will differ for R- and H-type in the stacked ²WSe₂/¹WSe₂. The electronic band hybridization involves antiparallel spin ordering of the spin-split bands for H-type stacking between the WSe₂ layers. On the other hand, for R-type stacking between the ²WSe₂/¹WSe₂, the spin-parallel bands undergo hybridization, enabling the electrons to scatter between WSe₂ layers^{29,30}. Such stacking-dependent band hybridization modifies the overall electronic band structure of the HTL system compared to the HBL system, thus creating additional indirect exciton transitions.

Since PLE addresses the absorption signatures of optically active material, we determine the actual absorption of our samples through reflectance measurements on HS1 and HS2, presented in Fig. 2d. The absorption features can be attributed to WSe₂ (~1.73 eV) and MoSe₂ (~1.66 eV) excitons. In addition, both samples show an enhanced absorption caused by the presence of the WSe₂ stacked bilayer, whereas MoSe₂ appears similar for HTL and HBL in HS1 and HS2. As shown in PLE results, a blueshift in absorption is also depicted in HS2, as shown in Fig. 2d. However, no relevant redshift was observed in sample HS1. Such a modification in ML resonances results in an energy shift for iX transition, as reported in refs. 22,31,32. However, a similar energy shift has not been noticed in our results shown in Fig. 1c. We explain this difference by considering that we compare arbitrary spots from HBL and HTL regions on the same sample (Supplementary Figs. 2 and 3 display several comparative data of HTL and HBL), and secondly, because the observed emission has a broad spectral width, more than 60 meV, which varies in every region of the sample. The PLE and reflectance contrast measurements are in good agreement with theoretical and experimental findings from refs. 29,30.

Discussion

The relative twist angle of stacked 2D materials strongly influences the band structure and, consequently, the exciton properties in TMDC heterostructures^{17,29,30,33,34}. Therefore, due to the tunable nature of such

heterostructures, the intra- and inter-layer exciton properties provide valuable insights into the wave function overlap and hybridization of electronic states. In order to provide fundamental microscopic insights into the PL and PLE enhancement, we performed first-principles DFT calculations of relevant high-symmetry stacking configurations (see Supplementary Fig. 5). Figure 3a shows the calculated band structures of the representative HBL and HTL systems, with the color code representing the layer localization of the wavefunction and the dashed arrows indicating the relevant optical transitions. Particularly for direct intra- and inter-layer transitions at the K valleys, the calculated values of the dipole matrix elements are presented in Supplementary Tables 3 and 4. Our results indicate that the dipole matrix elements for intralayer exciton transitions are rather robust and nearly independent of the twist angle and stacking. Comparing the iXs for the HBL cases, the dipole matrix element of the iX in the 38.2° case (HBL1 system in Fig. 3) is one order of magnitude weaker than the iX of the H_h^h case (HBL2 system in Fig. 3), which is consistent with the reduced PL intensities observed experimentally at large twist angles^{17,35–39}. For the iX species related to MoSe₂-²WSe₂ transitions, our DFT calculations reveal that the dipole matrix elements are strongly dependent on the stacking configuration. For the energetically favorable HTL stackings presented in Fig. 3, the MoSe₂-²WSe₂ iX has a comparable dipole matrix element to the MoSe₂-¹WSe₂ iX for the HTL2 case, but it shows a decrease of 2 orders of magnitude for the HTL1 case. To complement our analysis for direct iXs, we evaluated their binding energies, presented in Supplementary Table 6. We found that the binding energy of the MoSe₂-²WSe₂ iX is ~8 meV smaller than the MoSe₂-¹WSe₂ iX (which is nearly independent of the stacking details since the effective masses are essentially the same, as shown in Supplementary Table 5). Combining the energy separation of the WSe₂ valence bands (Supplementary Table 2) and the iX binding energies, we predict the MoSe₂-²WSe₂ iX energy to be ~15 (74) meV above the MoSe₂-¹WSe₂ iX in the HTL2 (HTL1) case. Therefore, we do not expect the MoSe₂-²WSe₂ iX to contribute to the observed PL enhancement, particularly in the HTL1 case. These findings are in line with recent investigations of trilayer systems composed of a natural bilayer MoSe₂ stacked on monolayer WSe₂²².

We now turn to the momentum-indirect transitions⁴⁰, involving the Q band (the conduction minima between Γ and K points) and the Γ band. In MoSe₂/WSe₂ HBL samples, transitions involving the Q and Γ bands seem to be strongly suppressed and not visible in the vast majority of the studied samples (with the exception of ref. 41), with strong support from magneto-optical characterizations highlighting the nature of direct K-K iX via their g-factors (see refs. 42,43 and references therein). In HTL systems, our DFT calculations predict that Q and Γ bands are energetically modified (Fig. 3a) due to the inclusion of the ²WSe₂ layer, and therefore momentum-indirect excitons are more likely to be present (indicated by the dashed orange lines in the HTL calculations of Fig. 3a). In addition to the energy increase (decrease) of Γ (Q) bands in the HTL systems, the layered character of the electronic wavefunction is also modified, as shown in Fig. 3b for the first conduction (bottom-most) and first valence (top-most) bands. While the layer character at the K bands remains nearly the same for HBL and HTL cases, the Q and Γ bands display a significant decrease of the MoSe₂ character from the HBL to HTL cases, accompanied by an increase of the WSe₂ character (with different contributions from ¹WSe₂ and ²WSe₂, depending on the particular HTL system, which in turn encodes the different coupling of R and H stacked WSe₂ homobilayers). We note that the twist angle-dependent coupling in WSe₂ homobilayers has been previously explored, e.g., in refs. 29,30, with distinct optical signatures arising from nearly 0° or 60°. Thus, momentum-indirect transitions with mixed intra- or inter-layer characters originating from the WSe₂ bilayer region influence the observed PL enhancement, particularly for the HTL1 case in which the direct MoSe₂-¹WSe₂ iX is further away in energy and has a weaker dipole matrix element.

At this point, the origin of the PL enhancement observed in our experiments can be traced to the interplay of distinct effects: (i) the increased absorption due to the second ²WSe₂ layer; (ii) the efficient charge transfer

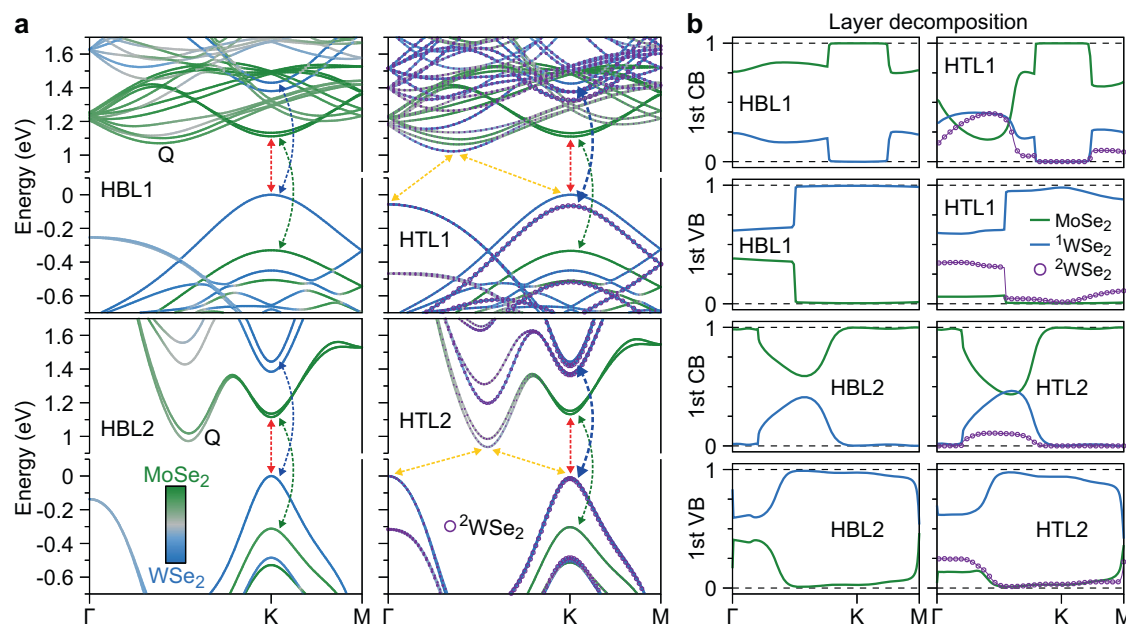


Fig. 3 | Electronic structure of heterobilayers and heterotrilayers. **a** Band structure calculations of selected HBL and HTL systems, with the color code representing the decomposition of the wavefunction into MoSe₂ (green) and WSe₂ (blue) layers. In HTL systems, the topmost WSe₂ layer is identified with the circles (the size is proportional to the layer contribution). Particularly, HBL1 refers to $\sim 38.2^\circ$ between MoSe₂ and ¹WSe₂, HBL2 refers to the 60° case with H_h^h stacking, HTL1 refers to a R_h^x stacking between ²WSe₂ and ¹WSe₂, and HTL2 refers to a H_h^h stacking between ²WSe₂ and ¹WSe₂. The arrows highlight the relevant optical transitions. In the HTL

systems, we identify the momentum-indirect excitons (K–Q and Γ –Q). The thicker arrow of the WSe₂ intralayer transitions in HTL cases indicates enhanced absorption. **b** Layer decomposition of the wavefunction for the first conduction band (CB) and first valence band (VB). The impact of ²WSe₂ is more pronounced at the Q and Γ bands (particularly reducing the contribution of MoSe₂), thus favoring momentum-indirect transitions. The band structures and layer decomposition of the other investigated structures are presented in Section IV of the SI.

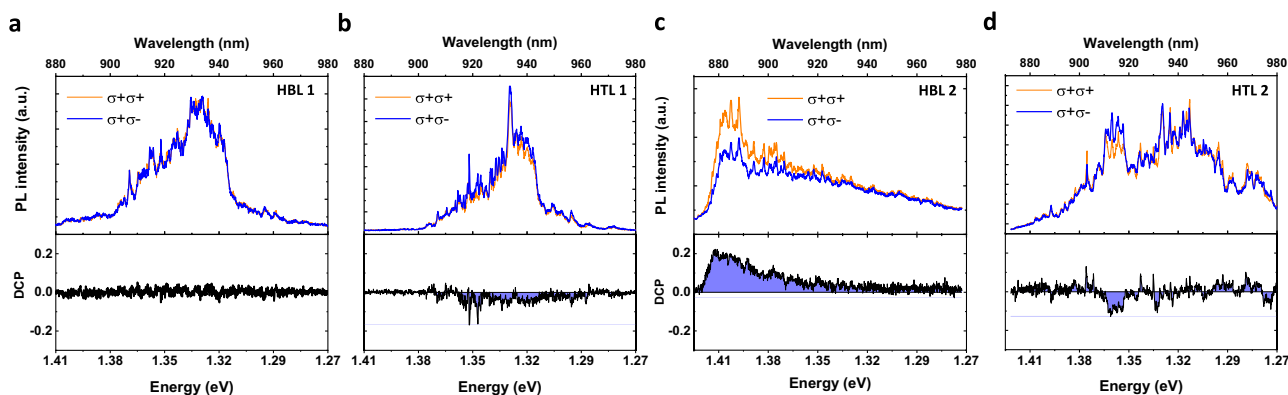


Fig. 4 | Polarization dependent photoluminescence and degree of circular polarization. Photoluminescence collected with right (σ^+) and left (σ^-) circular polarization upon a pulsed laser excitation with σ^+ polarization shown in the upper panel for **a** HBL1, **b** HTL1, **c** HBL2, and **d** HTL2 regions. The bottom panel shows the calculated DCP.

between the WSe₂ layers; and (iii) the appearance of momentum-indirect excitonic emission channels. The increased absorption and signatures of band hybridization are clearly observed via PLE and reflectance contrast measurements, shown in Fig. 2.

To provide further insight into the nature of the exciton emissions observed in the HBL and HTL samples, we investigate the polarization resolved PL, displayed in Fig. 4. In these measurements, we consider a resonant excitation to the A exciton of WSe₂ (1.72 eV) with σ_+ circularly polarized light. Following the excitation, only σ_- and σ_+ circularly polarized emission was selected and recorded. The degree of circular polarization, $DCP = (\sigma_- - \sigma_+)/(\sigma_- + \sigma_+)$, is shown in the lower panel of Fig. 4. In HBL1, the negligible value of the DCP (Fig. 4a) can be directly associated to the momentum mismatch introduced by the large twist angle of 44° . In HTL1, the marginal revival of the DCP (Fig. 4b) can be attributed to the phonon-mediated emission of momentum-indirect excitons already observed in

natural WSe₂ bilayers^{22,44,45} but now originating from a WSe₂ bilayer with 0° stacking. In the HBL2 sample, the large positive value of DCP (Fig. 4c) is consistent with the iX triplet state from the H_h^h stacking^{12,31,46–48}. Finally, the DCP of the HTL2 case (Fig. 4d) shows a negative value at the emission energy of ~ 1.36 eV with additional weak contributions at lower energy arising from the momentum-indirect excitons with stronger WSe₂ character. The negative DCP at ~ 1.36 eV seen in HTL2 indicates a reminiscent emission of the iX singlet state in the H_h^h stacking or even the iX between MoSe₂ and ²WSe₂, which has the same selection rules (see Supplementary Table 3). Lastly, based on our experimental and theoretical findings, we highlight the preferential stacking alignment of R_h^x for ²WSe₂/¹WSe₂ in the S1 system, which provides substantial emission enhancement even in the HBL system with large twist angles.

In conclusion, our theoretical and experimental study shows that mechanically stacked WSe₂/WSe₂/MoSe₂ HTL systems with varying twist

angles can lead to PL enhancement by up to 20 times in the HTL regions, compared to their HBL counterparts. Previous works on $\text{WSe}_2/\text{MoSe}_2$ HBL systems with large twist angles have shown that iXs display a very low emission intensity. This makes such HBL systems impracticable for detailed investigation and applications due to their large momentum mismatch as well as large interlayer separation, causing the reduced iX population. In contrast, our findings introduce an efficient and powerful platform for enhancing the exciton population and emission intensity. The recorded enhancement in the PL emission results from increased absorption and emission channels due to intentionally added WSe_2 on top of the twisted $\text{WSe}_2/\text{MoSe}_2$ HBL system. In a nutshell, our investigation demonstrates that the PL intensity in the twisted $\text{WSe}_2/\text{MoSe}_2$ systems can be enhanced and controlled by simply adding the additional layer of WSe_2 with an R- or H-type configuration. Furthermore, our first-principles calculations indicate that the interaction between the three layers facilitates the formation of additional momentum-indirect excitons that contribute to the enhancement of the emission in the HTL regions. This fundamental study of excitons in the HTL system deepens our current understanding of the physics of twisted TMDC heterostructures and paves the way for future experimental and theoretical investigations.

Methods

Sample fabrication

The multilayered TMDC samples were fabricated using mechanical exfoliation⁴⁹ and the dry-transfer method⁵⁰. For exfoliation of the MLs, commercially available crystals of MoSe_2 and WSe_2 are used along with Netto blue tape and Polydimethylsiloxane (PDMS). Bulk crystals of MoSe_2 and WSe_2 are mechanically exfoliated on the PDMS gel strip with the help of scotch tape. Next, the individual MLs are identified by optical contrast microscopy and PL spectroscopy at room temperature. Single crystalline MLs of MoSe_2 and WSe_2 are selected by observing the formed straight edges, at 60° or 120° , as an indication of crystal axes. For the first sample (HS1) fabrication, the MoSe_2 ML was transferred onto a 180 nm layer of SiO_2 deposited on Si substrate. During the stacking process, the WSe_2 ML was aligned to the edge of MoSe_2 ML, addressing 0° or 60° twist angles. The WSe_2 ML was partially brought in contact with the MoSe_2 monolayer until touching it, thus intentionally being retrieved from the substrate in order to split the WSe_2 ML into two parts. To fabricate the trilayer, the remaining WSe_2 ML, attached to the PDMS, is transferred onto the $\text{WSe}_2/\text{MoSe}_2$ heterobilayer. The nominal twist angle between the two WSe_2 was therefore 0° . To achieve top encapsulation, an exfoliated thin (~ 5 nm) hBN layer is transferred onto the heterotrilevel for both samples. Following a similar sample preparation method, a second sample (HS2) was achieved; however, in this case, the second WSe_2 monolayer transferred was obtained using another monolayer, and the angle between the $\text{WSe}_2/\text{WSe}_2$ bilayer was 60° .

Photoluminescence spectroscopy

The PL spectroscopy was used to measure the excitonic emission from the MLs and heterostructure systems at room temperature for identification of MLs as well as at low temperature to study the iX emission from HTL and HBL regions. For ML identification, a continuous wave excitation laser was used with a wavelength of 532 nm. Low-temperature measurements were conducted at 4 K using a close-cycle cryostat equipped with a high numerical aperture (NA = 0.81) objective lens. For low-temperature measurements, a wavelength-tunable picosecond mode lock pulsed laser was used as a source of excitation to perform the photoluminescence excitation measurements. For the PLE measurements, the iX emission intensity was recorded by tuning the laser from 705 to 790 nm while keeping the excitation power constant over the tuning range.

Second harmonic generation

The twist angle between the constituent layers of the samples HS1 and HS2 was determined by performing polarization-resolved second harmonic generation (SHG) measurements⁵⁶. The intensity as a function of the excitation laser polarization is recorded from the ML transferred on the

substrate, which was excited with a linearly polarized picosecond mode-locked laser. The TMDC ML is excited with a linearly polarized femtosecond mode-locked laser with a wavelength of 1313 nm. Then, the SHG intensity (at 556) as a function of excitation laser polarization is recorded from the ML transferred on the substrate. The characteristic intensity maxima show a sixfold symmetry, and each maximum indicates the armchair direction on the hexagonal crystal lattice of the associated TMDC ML. Comparing the SHG response from the constituent ML of the heterostructure system, the twist angle between the ML can be determined with high accuracy. To differentiate between R- or H-type stacking, we measured the SHG response of the HBL and the HTL regions. Reduction in intensity of SHG signal from the HBL region with respect to MLs indicates H-type stacking. Similarly, for stacked WSe_2 MLs, R-type stacking results in a higher SHG signal than H-type stacking as it leads to restored inversion symmetry⁵¹. The overall measurement and fitting error is in the range of 1° to 3° .

Density functional theory

We evaluate the electronic and optical properties of the HBL $\text{WSe}_2/\text{MoSe}_2$ and HTL $\text{WSe}_2/\text{WSe}_2/\text{MoSe}_2$ based on DFT using the all-electron full-potential linearized augmented plane-wave (LAPW) method within the Wien2k code⁵². We employ the Perdew–Burke–Ernzerhof⁵³ exchange–correlation functional with van der Waals interactions included via the D3 correction⁵⁴. The wave function expansion into atomic spheres takes into account orbital quantum numbers up to 10, and the plane-wave cut-off multiplied with the smallest atomic radii is set to 8. Spin–orbit coupling was included fully relativistically for core electrons, while valence electrons were treated within a second-variational procedure⁵⁵ with the scalar-relativistic wave functions calculated in an energy window up to 2 Ry. Self-consistency was achieved using a two-dimensional Monkhorst–Pack k-grid with 15×15 points, and the convergence criteria of $10^{-6} e$ for the charge and 10^{-6} Ry for the energy were used. We considered an average lattice parameter of 3.2855 Å for MoSe_2 and WSe_2 which amounts to an average and negligible strain of $\sim 0.1\%$ ⁴³. A vacuum region of 20 Å was considered to avoid interaction between the heterostructures replicas. The atomic positions were relaxed in the out-of-plane direction using a force convergence threshold of 10^{-4} Ry/Bohr. For sample HS1, we constructed a twisted supercell with an angle of $\sim 38.2^\circ$ between MoSe_2 and the first WSe_2 and investigated the effect of different R-type stackings between the first WSe_2 and second WSe_2 layer, namely the R_h^M and R_h^X stackings (R_h^M is known to be energetically unfavorable⁴³). The choice of a twist angle of $\sim 38.2^\circ$ provides a relatively small supercell to investigate the trilayer systems (totaling 63 atoms) while still capturing the momentum mismatch that reduces the oscillator strength of interlayer excitons (see Supplementary Tables 3 and 4), as seen in the real 44° sample. For sample HS2, we assumed the H_h^M stacking between MoSe_2 and the first WSe_2 (60° twist angle) and investigated the effect of different H-type stackings (H_h^M , H_h^M , and H_h^X) between the first WSe_2 and second WSe_2 layer. The details of the different stackings, as well as the structural parameters, are given in Supplementary Table 2. The dipole matrix element between valence and conduction band states at the K point is calculated as $\frac{\hbar}{m_0} \langle \nu, K | \mathbf{p} \cdot \hat{\alpha} | c, K \rangle$ for the LAPW basis set⁵⁶, in which $\hat{\alpha}$ encodes the light polarization (σ^+ , σ^- , and z). The calculated values of the dipole matrix elements for direct transitions are given in Supplementary Tables 3 and 4.

Exciton binding energies

The calculated binding energies for the interlayer excitons were obtained using the effective Bethe–Salpeter equation^{57,58} formalism, assuming non-interacting parabolic bands for electrons and holes^{59,60}. We consider the effective masses taken from DFT and the interlayer electrostatic potential obtained numerically by solving the Poisson equation in k -space, assuming the different regions with dielectric constants of $\epsilon(\text{MoSe}_2) = 16.8$ ⁶¹ and $\epsilon(\text{WSe}_2) = 15.3$ ⁶¹, $\epsilon(\text{SiO}_2) = 3.9$ ⁶², $\epsilon(\text{hBN}) = 4.5$ ⁶³, and the TMDCs with an effective thickness of 6.72 (6.78) for MoSe_2 (WSe_2), taken as twice the value of the physical thickness of the TMDC⁶². The calculated interlayer exciton potentials, effective masses, and binding energies are given in Supplementary Note 5.

Data availability

The data that support the findings of this work are available from the corresponding author upon reasonable request.

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Author contributions

C.C.P., B.R., and S.R. conceived and planned the experiments. C.C.P. and B.R. prepared the TMDC samples. C.C.P., B.R., and F.B.S. carried out the experiments. S.R. and L.M. supervised the experiments. C.C.P. and B.R. processed the experimental data and performed the analysis. P.E.F.J. developed the theory and performed the DFT calculations. J.F. supervised theoretical investigation. All authors discussed the results and contributed to the final paper.

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Competing interests

The authors declare no competing interests.

Additional information

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