

Defect-Dependent Optoelectronic Properties at a Molecular p-dopant/Monolayer WS₂ Interface

Jie Ma, Patrick Amsalem, Thorsten Schultz, Xiaomin Xu, and Norbert Koch*

Combining transition metal dichalcogenides (TMDCs) and molecular semiconductors is an attractive route for forming van der Waals heterostructures with optoelectronic properties not found in either component. Herein, the strong p-type molecular dopant, 1,3,4,5,7,8-hexafluoro-tetracyano naphthoquinodimethane (F₆TCNNQ), is utilized to form a van der Waals interface with a WS₂ monolayer chemical vapor deposition grown on sapphire, which is characterized with angle-resolved photoelectron and UV-visible absorption spectroscopy. The interface formed by F₆TCNNQ and the as-grown WS₂ monolayer (ML-WS₂) shows no sign of strong interaction or charge transfer. In contrast, defects formed by annealing of ML-WS₂ at 1000 K (*d*-ML-WS₂) induce strong n-type doping of the TMDC. Subsequent F₆TCNNQ adsorption on *d*-ML-WS₂ is then accompanied by pronounced charge transfer resulting in the formation of interface F₆TCNNQ anions and an interface optical transition at 1.5 eV, possibly attributed to an interlayer excitonic state. It is shown in the results that the presence of defects within TMDC monolayers can substantially modify not only the TMDC electronic properties, but also the ground and excited states of their interface with organic molecular dopants. This demonstrates an additional degree of freedom for designing tailored (opto-)electronic properties based on the combination of TMDCs and molecular semiconductors.

monolayer (ML) form, are semiconductors considered as potential materials for applications in next generation of optoelectronic devices,^[1] for example in thin-film transistors,^[2–5] photovoltaic cells,^[6,7] photo-detectors,^[8,9] and bio-inspired devices.^[10,11] Unlike graphene, showing semimetallic properties, the 2D TMDCs feature a tunable bandgap, which goes from indirect to direct by decreasing the number of layers down to one ML,^[12,13] associated with unique structural^[14] and optoelectronic properties.^[15–17] Remarkable features like rich excitonic states,^[18,19] clean surfaces,^[20,21] and controllable microstructure provide the opportunities for the fabrication of heterostructures built in conjunction with organic semiconductors (OSCs) to combine the advantages of the two distinct class of material.^[22,23] Especially, organic molecule/ML-TMDC heterostructures can exhibit novel hybrid optoelectronic properties^[22,24] and these naturally depend strongly on the ground-state electronic structure of the corresponding interface.^[25,26]

1. Introduction

The 2D transition metal dichalcogenides (TMDCs) with formula MX₂ (e.g., M = Mo, W and X = S, Se), particularly in their

Recent studies, both theoretical and experimental have demonstrated that interfacial excitonic transitions can occur at molecule/ML-TMDC interfaces.^[22,24–27] For example, charge-transfer (CT) excitons were observed at tetracene/WS₂^[28,29] and zinc-phthalocyanine/MoS₂^[30] heterostructures and were attributed to particular CT processes occurring at the OSC/TMDC interface upon photoexcitation. Studies available to date are mostly limited to the interfacial photoexcitation dynamics at molecule/pristine ML-TMDC interfaces. However, TMDCs exhibit a range of structural defects such as sulfur vacancies (V_S), which are the most abundant defects as their formation requires the least activation energy.^[31,32] Importantly, such defects can strongly impact the electronic structure and excited states of TMDCs.^[31,33–35] Controlling and understanding the impact of defects on the electronic properties of TMDCs, a field of research known as defect engineering, is therefore of fundamental importance. Meanwhile, ground-state CT processes were demonstrated at defective TMDC/OSC interfaces using small molecules with large electron affinity (EA), giving rise to a CT density of states (DOS) within the bandgap of both materials and modifying the TMDC optical properties, notably via the tuning of the trion-to-exciton ratio.^[36–39] Here, we aim at understanding how the presence of defects in an ML-TMDC can impact both the ground and excited states of an OSC/ML-TMDC interface. It is reasonable to

J. Ma, P. Amsalem, X. Xu, N. Koch
 Institut für Physik & IRIS Adlershof
 Humboldt Universität zu Berlin
 12489, Germany
 E-mail: norbert.koch@physik.hu-berlin.de

J. Ma, T. Schultz, N. Koch
 Helmholtz Zentrum Berlin für Materialien und Energie GmbH
 12489, Germany

X. Xu
 Tsinghua-Berkeley Shenzhen Institute (TBSI)
 Tsinghua University
 518055, China

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/pssa.202300106>.

© 2023 The Authors. physica status solidi (a) applications and materials science published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/pssa.202300106

assume that the presence of defect-related states in the TMDC influence also the ground-state electronic properties of the interface, and may favor the emergence of interface excited states at the OSC/ML-TMDC interface. Relating the ground-state electronic properties and the excited states of such systems by assessing their DOS and the corresponding optoelectronic transitions should therefore provide important insights in the fundamental processes taking place at these interfaces.

In this contribution, we investigated the optoelectronic properties of an interface combining a strong organic molecular p-dopant, 1,3,4,5,7,8-hexafluoro-tetracyano naphthoquinodimethane (F_6TCNNQ), and a WS_2 monolayer (ML- WS_2) supported on a sapphire substrate using angle-resolved photoelectron spectroscopy (ARPES) and UV-vis absorption spectroscopy. F_6TCNNQ , a strong electron acceptor with an EA of ≈ 5.6 eV,^[40] was deposited on a chemical vapor deposition (CVD)-grown ML- WS_2 featuring initially a small density of defects, and we compare this to the situation when a CVD grown ML- WS_2 with a much higher density of defects, achieved by post-growth annealing in ultrahigh vacuum (UHV) at 900–1000 K, is used. The ARPES spectra of the highly defective WS_2 monolayer (d -ML- WS_2) show an additional DOS at the Fermi level, attributed to the filling of the WS_2 conduction band (CB). In turn, for the non-annealed ML- WS_2 sample, ARPES measurements were prevented by strong sample charging, suggesting that the delocalized charge carriers observed for the highly defective ML are indeed either absent or marginal in the pristine ML- WS_2 . Consecutive ARPES measurements demonstrate the presence of ground-state CT at the F_6TCNNQ/d -ML- WS_2 interface, and the absorption spectra show a series of peaks that are absent when F_6TCNNQ is deposited on the pristine ML- WS_2 . One set of peaks is attributed to transitions of F_6TCNNQ anions, which were identified by ARPES. Notably, an additional absorption peak is observed in between those of the WS_2 A-exciton and the F_6TCNNQ anions, which is suggested as an interlayer molecule-TMDC transition. These results demonstrate that defect engineering of TMDCs can not only modify the optoelectronic properties of the MLs itself but also of their interfaces with organic molecules.

2. Results

2.1. Electronic Structure of the F_6TCNNQ /Annealed WS_2 (d -ML- WS_2) Interface

Throughout this work, we present the ARPES spectra taken at the Γ -, Q -, and K -points of the ML- WS_2 Brillouin zone (BZ) for the defective d -ML- WS_2 and of F_6TCNNQ sequentially deposited on d -ML- WS_2 . We note that although the sample is polycrystalline (in plane) and ARPES thus averages over all directions of the BZ, particularly high photoemission intensity is detected along the high symmetry directions due to the high momentum DOS (k -DOS) along those lines. Therefore, the ARPES spectra taken at any $k_{||}$ represent almost exclusively a superposition of the energy distribution curves (EDCs) along the Γ - Q - K and Γ - M lines at the corresponding $k_{||}$ value, which allows band tracking and comparison with the known band structure along these directions.^[41] We also remark that ARPES measurements of

the as-grown ML- WS_2 and of the F_6TCNNQ /ML- WS_2 interfaces were precluded by pronounced sample charging. However, we note that measurements of such ML- WS_2 when transferred to a conductive substrate (e.g., HOPG) displayed the expected band structure, with the valence band maximum (VBM) at the K -point, which is responsible for the direct bandgap of ML- WS_2 .^[42] Such direct bandgap on the produced sample is here confirmed by the absorption spectrum described in the next section.

ARPES measurements of F_6TCNNQ sequentially grown on d -ML- WS_2 /sapphire were possible, because the annealed ML- WS_2 had sufficiently high conductivity to avoid sample charging upon photoionization. This is likely a result of the presence of defects (e.g., V_S), which leads to strong n-type doping of the WS_2 . **Figure 1** depicts a) the secondary electron cutoff (SECO) spectra, b) EDCs at Γ , and c) the EDCs at K upon increasing nominal F_6TCNNQ coverage. From the SECO spectra, we determined the sample work function evolution upon molecule deposition, which changes from ≈ 4.3 eV for bare d -ML- WS_2 to 5.3 eV for an (sub-) ML F_6TCNNQ (for 1 and 2 Å nominal F_6TCNNQ coverage), and shows an additional 0.1 eV increase for the 10 nm F_6TCNNQ film. When inspecting the valence band spectra at Γ and K of the bare d -ML- WS_2 , we first observe that the VBM onset is located at K at 1.72 eV binding energy (BE), demonstrating electronic properties in line with those of an ML with strong n-type character. We observe a rigid shift of 0.6 eV to lower BE of the TMDC features upon F_6TCNNQ deposition. The work function increase seen upon F_6TCNNQ deposition indicates the formation of an interface dipole with the negative pole located in the molecular layer, correlating with a ground-state electron transfer from d -ML- WS_2 to F_6TCNNQ . Consistently, the VBM shift upon F_6TCNNQ deposition is attributed to de-doping of the initially strongly n-type d -ML- WS_2 .

A closer look at the electronic states in the Fermi-level region is provided in **Figure 2**, which depicts the EDCs of the clean and the 1 Å F_6TCNNQ -covered d -ML- WS_2 taken at a) Γ , b) Q , and c) K points of the BZ of the TMDC. The Γ and K spectra of pristine d -ML- WS_2 are featureless in this energy region, in contrast to the spectrum at Q , which therefore indicates the presence of dispersive states at this point of the BZ. Density-functional theory calculations of the WS_2 band structure yield a CB minimum at the K -point and a local CB minimum at the Q -point which is very close in energy to the CBM.^[43] Notably, the here-observed intensity at Q (while absent at K) and its dispersive character corresponds to that of the CB minimum at Q (see Figure S3, Supporting Information). This demonstrates the presence of delocalized charge carriers within the d -ML- WS_2 ^[44] whose band structure is strongly renormalized, possibly by the effect of strain at the interface with sapphire and yielding a CB minimum at the Q -point.^[43] We note that such band renormalization is still observed after transfer of a WS_2 film grown on sapphire to another sapphire followed by annealing in vacuum as necessary to perform the ARPES measurements (Figure S3, Supporting Information). Upon deposition of F_6TCNNQ , two interface-related features with peak maxima at ≈ 0.4 eV (peak A) and 1.0 eV (peak B) emerge and are visible at all $k_{||}$. The absence of dispersion of these electronic states is a clear indication of their molecular character. They are arising because of electron transfer from the ML- WS_2 to the OSC, resulting in the formation

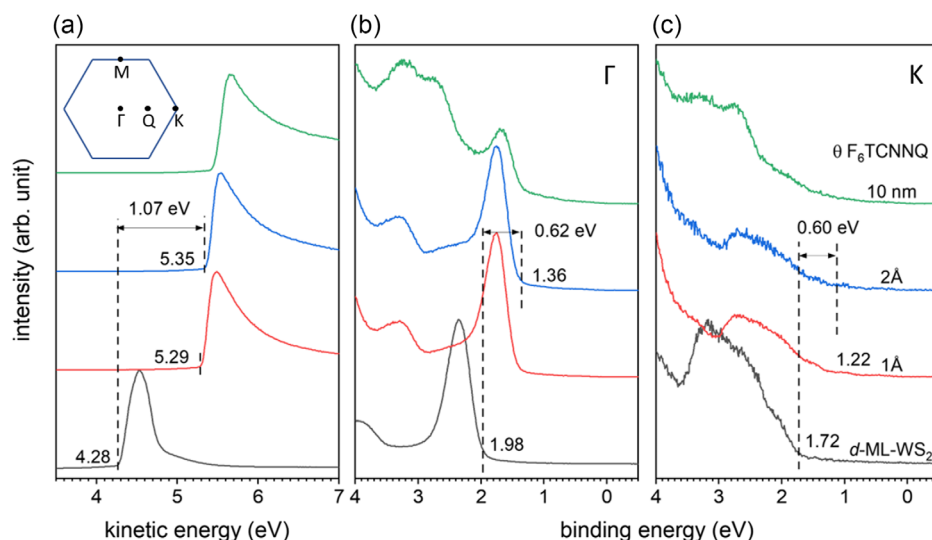


Figure 1. Thickness-dependent angle-resolved photoelectron spectroscopy (ARPES) spectra of 1,3,4,5,7,8-hexafluoro-tetracyano naphthoquinodimethane (F_6TCNNQ)/ d -ML- WS_2 /sapphire. a) Secondary electron cutoff (SECO) and valence band spectra measured at b) Γ and c) K . Inset: Brillouin zone of WS_2 and notable high-symmetry points.

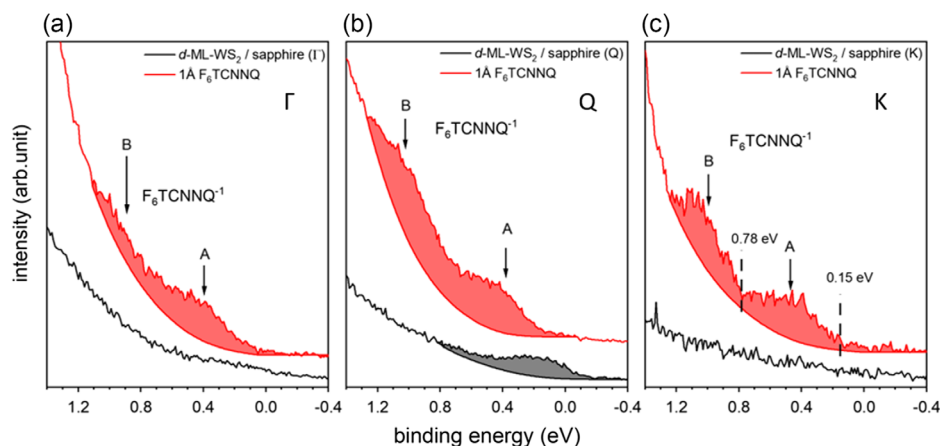


Figure 2. ARPES spectra of the Fermi-level region of 1 Å F_6TCNNQ / d -ML- WS_2 /sapphire and bare d -ML- WS_2 measured at a) Γ , b) Q , and c) K of the ML- WS_2 BZ.

of molecular anions.^[36,37] Consistent with previous studies, charging of the F_6TCNNQ molecules by CT leads to the splitting by an energy U , the Coulomb repulsion, of the neutral F_6TCNNQ lowest unoccupied molecular orbital (LUMO) level into a singly occupied molecular orbital (SOMO) level and a singly unoccupied molecular orbital (SUMO) level.^[36,45,46] In the spectra shown here, the peak A with its maximum at ≈ 0.4 eV is attributed to the SOMO. The peak B with its maximum at ≈ 1.0 eV is assigned to stem from the highest occupied molecular orbital (HOMO) level of the former neutral molecule, whose ionization energy is strongly renormalized due to the additional electron accommodated by the anion. This ground-state CT is driven by the energy difference between the low work function (4.3 eV) of d -ML- WS_2 and the high F_6TCNNQ EA of 5.6 eV. Additionally, it is also observed that the states representative

of the CBM at the Q -point are depopulated upon F_6TCNNQ adsorption, confirming thereby the ground-state CT between the TMDC and the OSC. Finally, as shown in Supporting Information, further depleting the CB by depositing additional F_6TCNNQ decreases the conductivity of the sample as slight sample charging starts to occur already at 2 Å coverage (see Figure S4, Supporting Information).

2.2. Optical Properties of the F_6TCNNQ /(d -)ML- WS_2 Interface

We now assess optical excitations of the F_6TCNNQ /(d -)ML- WS_2 interface from the UV-vis measurements presented in Figures 3 and 4. First, the UV-vis spectrum of the pristine (not annealed) ML- WS_2 on sapphire features the expected A-

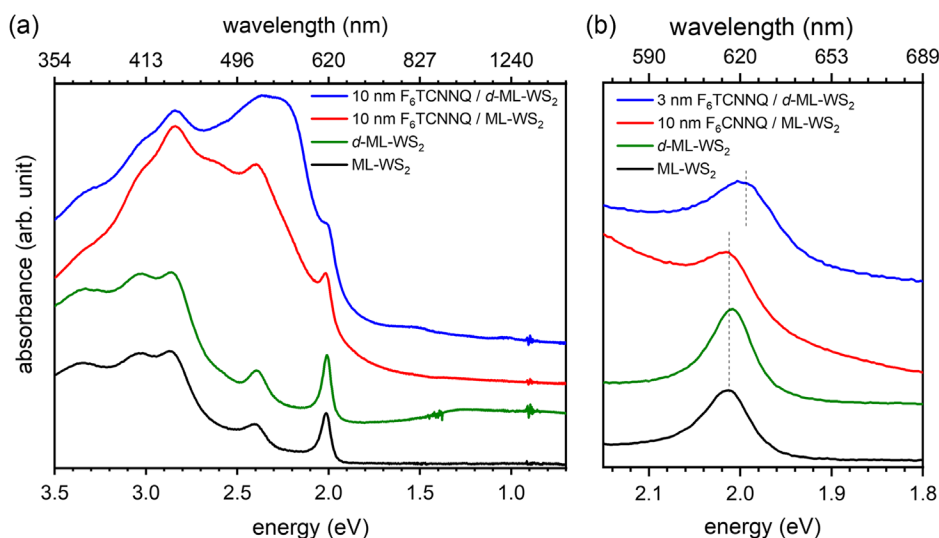


Figure 3. a) Wide-range UV-vis spectra of ML-WS₂ and *d*-ML-WS₂ before and after deposition of 10 nm F₆TCNNQ. b) Zoom in the energy region of the A-exciton. Note that in (b) a 3 nm F₆TCNNQ film was deposited on *d*-ML for a better visibility of the exciton.

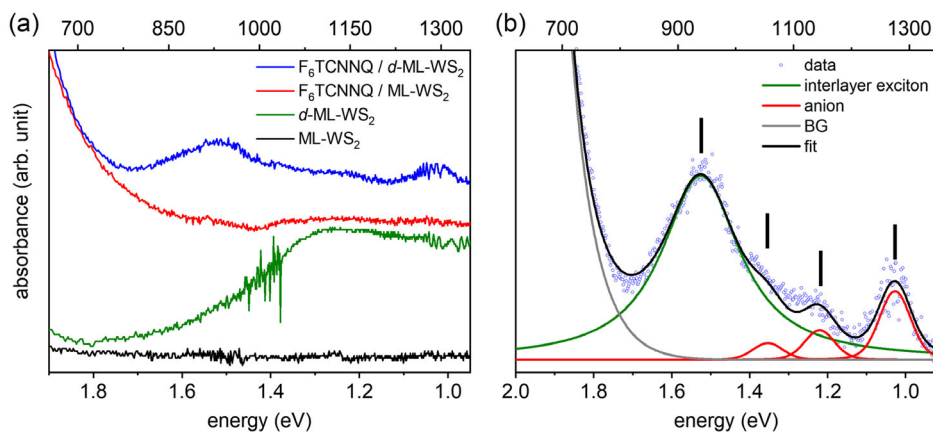


Figure 4. a) Zoom in the low-energy region UV-vis spectra of ML-WS₂ and *d*-ML-WS₂ before and after deposition of 10 nm F₆TCNNQ. b) Fit of the F₆TCNNQ/*d*-ML-WS₂ spectra.

exciton as a first intense and sharp absorption peak at ≈ 2.01 eV. Below the absorption edge of the A-exciton, no features are observed. The UV-vis spectrum of 10 nm F₆TCNNQ grown on the pristine ML-WS₂ mostly consists of a linear superposition of the absorption spectrum of pristine F₆TCNNQ, with its main feature at 2.4 eV,^[47] and of the bare ML-WS₂ film as shown in Figure S5, Supporting Information. Note that the small deviation from a perfect linear superposition may result from different orientation of the molecules on the reference quartz substrates and on WS₂, but also from imperfection of the subtraction procedure. The fact that the optical characteristics of F₆TCNNQ/ML-WS₂ are close to those of its pristine components is consistent with a weak OSC-TMDC interaction, involving no apparent ground-state CT between the components, because no (or very few) charge carriers are available in the ML-WS₂. Annealing at 900–1000 K of ML-WS₂ for 24 h in UHV was performed to produce the defective *d*-ML-WS₂ sample with an expected higher density of V_S.^[48] The corresponding UV-vis spectrum of *d*-ML-WS₂ then exhibits

similar features as the not annealed ML-WS₂, both in lineshape and energy position. However, we do not observe any (sharp) defect-related feature just below (i.e., 0.2–0.3 eV) the A-exciton, in contrast to previous in situ photoluminescence studies;^[34] this is likely due to variations in detailed sample handling. Another noticeable difference is the observation of a broad and asymmetric intensity peaking at about 1.35 eV and extending toward the low energy side. Such intensity apparently stems from interband transitions apparently involving the presence of defects (see discussion in Supporting Information, Section 5). The UV-vis spectrum of the F₆TCNNQ/*d*-ML-WS₂ sample displays a redshifted (15 meV) and broadened A-exciton peak, which is readily visible for a slightly thinner (nominally 3 nm) F₆TCNNQ film as shown in Figure 3b. This redshift compares consistently with a more intrinsic TMDC film, which is here achieved by de-doping upon F₆TCNNQ adsorption.^[49] Furthermore, a series of sub-bandgap peaks below 1.8 eV can be seen, those being absent for all other samples. In more detail, Figure 4 shows the spectra zoomed in

the low energy range (0.9–2.0 eV) after subtracting a background due to Rayleigh scattering. In this energy range, the UV–vis spectrum of ML-WS₂ is basically featureless as is that of F₆TCNNQ/ML-WS₂. For F₆TCNNQ/*d*-ML-WS₂, the UV–vis spectrum exhibits four peaks between 1.8 and 1.0 eV. As demonstrated by ARPES, ground-state CT between *d*-ML-WS₂ and F₆TCNNQ leads to negatively charged molecules and concomitantly to the de-doping of *d*-ML-WS₂. The formation of molecular anions is here confirmed by the series of absorption peaks at ≈1.02, 1.21, and 1.38 eV, the typical signature of F₆TCNNQ[−] reported in Figure S6, Supporting Information, and in literature.^[47,50] More precisely, the peak at 1.02 eV corresponds to the 0–0 transition, which is followed by the two vibronic progressions at 1.21 and 1.38 eV. In addition, a further peak at ≈1.52 eV is observed. This peak cannot be ascribed to molecular anions or *d*-ML-WS₂. Similar feature have been reported for F₆TCNNQ-related doping of polymer films or carbon nanotubes and were attributed to the formation of anion dimers. In the present case, such interpretation cannot be excluded though the formation anion dimer with π – π stacking appears less likely as CT is most likely limited to the interface F₆TCNNQ molecules, those lying flat on the surface.^[37,51,52] Another explanation is that this optical transition relates to an interface feature, that is, an interlayer excitonic state, whose possible origin is discussed later. We finally remark that the defect-related absorption band below 1.5 eV of *d*-ML-WS₂ is quenched upon F₆TCNNQ deposition. The quenching of this presumably defect-related band of *d*-ML-WS₂, together with the emptying of the electron pocket at *Q* upon F₆TCNNQ deposition thus suggests that the CB near the minimum at *Q* was involved in the initial emergence of the broad, defect-related, absorption band.

3. Discussion

To examine which levels could be involved in the interlayer exciton suggested earlier, a correlation the absorption features with an energy-level diagram based on the ARPES results appears useful. Schematic diagrams of the frontier energy levels of (*d*-)ML-WS₂ and F₆TCNNQ, and their interfaces are shown in Figure 5. There, the BE of the levels is referred to the Fermi level, and in addition the exciton energies determined from the UV–vis measurements are provided. First, Figure 5a depicts the optical

transition due to the A exciton in (*d*-)ML-WS₂ at the *K*-point, assuming an exciton BE of 0.3 eV,^[53] and the filling of the CB at the *Q*-point. The HOMO and LUMO levels of the neutral F₆TCNNQ “before contact,” that is, assuming vacuum-level alignment with respect to that of (*d*-)ML-WS₂, are further displayed in Figure 5b. As F₆TCNNQ has an EA of 5.6 eV,^[40] its LUMO (onset) is then found about 1.3 eV below the Fermi level, but well above the *d*-ML-WS₂ VBM. The F₆TCNNQ electronic gap was determined by the gap between the onset of the HOMO and LUMO as observed by direct and inverse photoemission to be 1.9 eV.^[40] Note that this electronic gap is actually smaller than the optical gap, probably because the absorption peak of a molecule represents the joint DOS (JDOS) of the material. Therefore, for a consistent interpretation of the UV–vis spectra with respect to the energy levels, it is preferable to consider the (single particle) HOMO and LUMO peak maxima of F₆TCNNQ at 8.4 and 5.3 eV (with respect to the vacuum level),^[40] respectively, as done in Figure 5. As the ionization energy from the VBM of (*d*-)ML-WS₂ is expected to remain mostly independent of electron doping, the relative energy-level alignment of F₆TCNNQ/(*d*-)ML-WS₂ before contact eventually relates to that of the F₆TCNNQ/ML-WS₂ interface, for which no CT occurs after contact due to the lack of available charge carriers. For the F₆TCNNQ/*d*-ML-WS₂ interface, electron transfer from the CB at *Q*, leading to the formation of molecular anions, strongly renormalizes the F₆TCNNQ energy levels at the very interface as shown in Figure 5c. The HOMO and SOMO energies are indicated with respect to their peak maxima as determined from ARPES. The SUMO is here positioned 0.6 eV above the Fermi level, by assuming a Coulomb repulsion energy *U* of 1 eV.^[46] The diagram suggests that the 0–0 optical transition of the anion is consistent with a HOMO–SUMO transition assuming a (screened) exciton BE in the range of 0.6 eV. Because of the de-doping of *d*-ML-WS₂ following the CT, we found from ARPES that the WS₂ VBM and CBM after F₆TCNNQ adsorption are then located at 1.4 and −0.8 eV BE, respectively. We can now tentatively attribute the origin of the 1.5 eV interface optical transition based on the energy difference of the F₆TCNNQ and WS₂ energy levels, leaving aside the other interpretation of anion dimer formation as discussed earlier. Considering an interlayer exciton BE in the range of ≈0.3 eV,^[29] we assess that an interlayer exciton could result (within 0.1 eV) from a transition between the

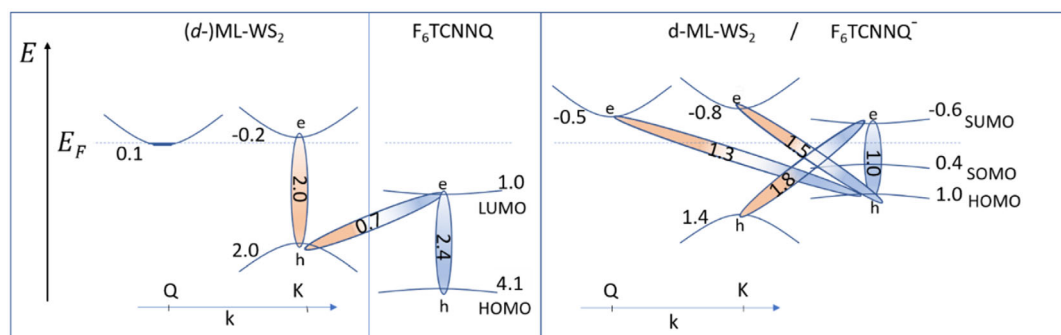


Figure 5. Energy-level alignment and possible optical transitions. The energy levels (solid lines) are defined by their peak maxima as determined from the (direct and inverse) photoemission. The displayed interlayer optical transitions account for an exciton binding energy of 0.3 eV. In this diagram, the possible transitions of F₆TCNNQ anion dimer discussed in the text are not shown.

F₆TCNNQ HOMO and the WS₂ CB. Note that in this scenario, we did not account for the possibility of transitions between localized WS₂ defect states and F₆TCNNQ anions because of the lack of direct observation of the former.

Finally, we comment on why an interlayer exciton could occur at the *d*-ML-WS₂/F₆TCNNQ interface but not at the pristine ML-WS₂/F₆TCNNQ one. First, we note that the lack of observation of an interlayer exciton at the pristine ML-WS₂/F₆TCNNQ may be related to the minimum energy accessible in these experiments (0.7 eV). Looking at the energy diagram and accounting for an exciton BE of 0.3 eV, one might expect an interlayer exciton with an absorption energy of ≈ 0.7 eV, which was at the limit of the experimentally accessible energy range and might have not been observed for this reason. Another possible explanation for the lack of interlayer exciton at the ML-WS₂/F₆TCNNQ interface is that the coupling between the organic molecules and the TMDC wave functions is so weak that it prevents the formation of interlayer excited states. In contrast, we reason that the interface dipole moment resulting from the CT at the *d*-ML-WS₂/F₆TCNNQ interface favors the formation of interlayer excitons, eventually with the electron located in the WS₂ and the hole in the molecule as proposed earlier. Last but not least, the (localized) defect states, though not seen here, may also play a role in the presently observed hybrid transition.

4. Conclusions

In this work, we demonstrated that the interaction between a strong p-dopant OSCs and ML-WS₂ is strongly dependent on post-growth treatment of the TMDC and its related defect formation. Here, the interaction between an as-grown WS₂ ML and F₆TCNNQ molecules is characteristic of a physisorptive adsorption and does not involve noticeable ground-state CT. In situ post-growth annealing of the WS₂ ML results in strong n-type doping. Because of the now available charge carriers in the annealed WS₂ ML, pronounced ground-state electron transfer to the subsequently deposited organic molecular layer is observed. The accordingly renormalized interface ground-state electronic structure then enables a modification of the optical properties of the material combination, with the notable emergence of an absorption peak possibly resulting from the formation of F₆TCNNQ anion dimers or from an interlayer excitonic state, which deserves further studies to be clarified. This shows that the optoelectronic properties of van der Waals systems formed by TMDCs and OSCs can be tuned by defect engineering and it opens new opportunities to investigate the relation of excited states versus ground states at such interfaces.

5. Experimental Section

WS₂ ML films were grown by CVD on sapphire according to the procedure detailed in Supporting Information (Figure S1, Supporting Information). The employed CVD parameters yielded the formation of a continuous WS₂ ML on sapphire with beyond 90% area coverage and less than 2% multilayer contributions (see Figure S2, Supporting Information). This film morphology warranted sufficient charge-carrier percolation paths for performing ARPES measurements without sample charging, and provided a sufficiently high conductivity of the ML-WS₂ and good electrical contact using metal clamps were assured.

F₆TCNNQ (Novaled GmbH) was deposited in UHV from a resistively heated crucible in a preparation chamber that was connected to the ARPES analysis chamber. The nominal molecular coverage was determined with a quartz crystal microbalance. The ARPES measurements were performed at room temperature in an analysis chamber (base pressure of 2×10^{-10} mbar) equipped with a Specs Phoibos 100 hemispherical electron analyzer and using the He I radiation provided by a monochromated helium discharge lamp (consisting of an HIS-13 lamp mounted on a VUV5046 UV monochromator), both from ScientaOmicron.

Optical absorption spectroscopy was performed in air using a Lambda 950 UV/vis/NIR spectrophotometer (Perkin Elmer Inc.). Measurements in solution were performed in dichloromethane (DCM) against a DCM-filled reference cuvette. The solid-state samples were measured against an uncoated sapphire glass slide.

Before deposition of F₆TCNNQ on ML-WS₂, the substrate was heated in UHV at ≈ 600 K to desorb the surface contaminants and to not induce the sample n-doping. The sample was then annealed in UHV at ≈ 900 – 1000 K before to desorb the molecular film and to produce *d*-ML-WS₂, before being measured by ARPES and UV-vis spectroscopy. Before deposition of F₆TCNNQ on *d*-ML-WS₂, the substrate was again heated more briefly at ≈ 900 – 1000 K to get rid of the surface contamination and potentially chemisorbed oxygen.

Supporting Information

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

Acknowledgements

This work was funded by the Deutsche Forschungsgemeinschaft (DFG), Project No. 182087777 (SFB 951). The authors thank Dr. Andreas Opitz for fruitful discussion and for providing the spectrum shown in Figure S5b, Supporting Information. Qiang Wang is also gratefully acknowledged for providing the sample used for the ARPES measurements in Figure S3. [Correction added after publication 10 January 2024: Article title was corrected.]

Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords

charge transfer, defect engineering, interlayer exciton, organics, photoemission, TMDC, UV-Vis spectroscopy

Received: February 15, 2023

Revised: April 29, 2023

Published online: July 14, 2023

- [1] H. Tian, M. Chin, S. Najmaei, Q. Guo, F. Xia, H. Wang, M. Dubey, *Nano Res.* **2016**, 9, 1543.
- [2] Y.-J. Kwack, T. T. T. Can, W.-S. Choi, *npj 2D Mater. Appl.* **2021**, 5, 84.
- [3] G. Baek, S. Seo, D. Hahm, W. Bae, J. Kwak, S. Jin, *Adv. Electron. Mater.* **2021**, 7, 2100535.

- [4] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, *Nat. Nanotechnol.* **2011**, 6, 147.
- [5] A. Dodda, D. Jayachandran, A. Pannone, N. Trainor, S. P. Stepanoff, M. A. Steves, S. S. Radhakrishnan, S. Bachu, C. W. Ordenez, J. R. Shallenberger, J. M. Redwing, K. L. Knappenberger, D. E. Wolfe, S. Das, *Nat. Mater.* **2022**, 21, 1379.
- [6] T. A. Shastri, I. Balla, H. Bergeron, S. H. Amsterdam, T. J. Marks, M. C. Hersam, *ACS Nano* **2016**, 10, 10573.
- [7] S. Roy, Z. Hu, S. Kais, P. Bermel, *Adv. Funct. Mater.* **2021**, 31, 2100387.
- [8] S. Zhang, X. Wang, Y. Chen, G. Wu, Y. Tang, L. Zhu, H. Wang, W. Jiang, L. Sun, T. Lin, H. Shen, W. Hu, J. Ge, J. Wang, X. Meng, J. Chu, *ACS Appl. Mater. Interfaces* **2019**, 11, 23667.
- [9] J. F. Gonzalez Marin, D. Unuchek, K. Watanabe, T. Taniguchi, A. Kis, *npj 2D Mater. Appl.* **2019**, 3, article no. 14.
- [10] D. Jayachandran, A. Oberoi, A. Sebastian, T. H. Choudhury, B. Shankar, J. M. Redwing, S. Das, *Nat. Electron.* **2020**, 3, 646.
- [11] A. Dodda, D. Jayachandran, S. Subbulakshmi Radhakrishnan, A. Pannone, Y. Zhang, N. Trainor, J. M. Redwing, S. Das, *ACS Nano* **2022**, 16, 20010.
- [12] K. F. Mak, C. Lee, J. Hone, J. Shan, T. F. Heinz, *Phys. Rev. Lett.* **2010**, 105, 136805.
- [13] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C. Y. Chim, G. Galli, F. Wang, *Nano Lett.* **2010**, 10, 1271.
- [14] X. Li, J. Shan, W. Zhang, S. Su, L. Yuwen, L. Wang, *Small* **2017**, 13, 1602660.
- [15] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano, *Nat. Nanotechnol.* **2012**, 7, 699.
- [16] D. Ovchinnikov, A. Allain, Y. S. Huang, D. Dumcenco, A. Kis, *ACS Nano* **2014**, 8, 8174.
- [17] C. Cong, J. Shang, Y. Wang, T. Yu, *Adv. Opt. Mater.* **2018**, 6, 1700767.
- [18] Z. Ye, T. Cao, K. O'Brien, H. Zhu, X. Yin, Y. Wang, S. G. Louie, X. Zhang, *Nature* **2014**, 513, 214.
- [19] M. G. Harats, J. N. Kirchhof, M. Qiao, K. Greben, K. I. Bolotin, *Nat. Photonics* **2020**, 14, 324.
- [20] M. Okada, T. Sawazaki, K. Watanabe, T. Taniguchi, H. Hibino, H. Shinohara, R. Kitaura, *ACS Nano* **2014**, 8, 8273.
- [21] K. S. Novoselov, A. Mishchenko, A. Carvalho, A. H. Castro Neto, *Science* **2016**, 353, aac9439.
- [22] N. Mutz, S. Park, T. Schultz, S. Sadofev, S. Dalgleish, L. Reissig, N. Koch, E. J. W. List-Kratochvil, S. Blumstengel, *J. Phys. Chem. C* **2020**, 124, 2837.
- [23] D. Jariwala, T. J. Marks, M. C. Hersam, *Nat. Mater.* **2016**, 16, 170.
- [24] M. Gobbi, E. Orgiu, P. Samorì, *Adv. Mater.* **2018**, 30, 1706103.
- [25] J. Krumland, C. Cocchi, *Electron. Struct.* **2021**, 3, 044003.
- [26] I. Gonzalez Oliva, F. Caruso, P. Pavone, C. Draxl, *Phys. Rev. Mater.* **2022**, 6, 054004.
- [27] J. Choi, H. Zhang, J. H. Choi, *ACS Nano* **2016**, 10, 1671.
- [28] T. Zhu, L. Yuan, Y. Zhao, M. Zhou, Y. Wan, J. Mei, L. Huang, *Sci. Adv.* **2018**, 4, eaao3104.
- [29] J. J. P. Thompson, V. Lumsargis, M. Feierabend, Q. Zhao, K. Wang, L. Dou, L. Huang, E. Malic, *Nanoscale* **2023**, 15, 1730.
- [30] T. R. Kafle, B. Kattel, S. D. Lane, T. Wang, H. Zhao, W. L. Chan, *ACS Nano* **2017**, 11, 10184.
- [31] A. Singh, A. K. Singh, *Phys. Rev. B* **2019**, 99, 121201.
- [32] S. Haldar, H. Vovusha, M. K. Yadav, O. Eriksson, B. Sanyal, *Phys. Rev. B Condens. Matter Mater. Phys.* **2015**, 92, 235408.
- [33] K. Greben, S. Arora, M. G. Harats, K. I. Bolotin, *Nano Lett.* **2020**, 20, 2544.
- [34] E. Mitterreiter, B. Schuler, A. Micevic, D. Hernangómez-Pérez, K. Barthelmi, K. A. Cochrane, J. Kiemle, F. Sigger, J. Klein, E. Wong, E. S. Barnard, K. Watanabe, T. Taniguchi, M. Lorke, F. Jahnke, J. J. Finley, A. M. Schwartzberg, D. Y. Qiu, S. Refaely-Abramson, A. W. Holleitner, A. Weber-Bargioni, C. Kastl, *Nat. Commun.* **2021**, 12, 3822.
- [35] C. Kastl, R. J. Koch, C. T. Chen, J. Eichhorn, S. Ulstrup, A. Bostwick, C. Jozwiak, T. R. Kuykendall, N. J. Borys, F. M. Toma, S. Aloni, A. Weber-Bargioni, E. Rotenberg, A. M. Schwartzberg, *ACS Nano* **2019**, 13, 1284.
- [36] S. Park, T. Schultz, X. Xu, B. Wegner, A. Aljarb, A. Han, L. J. Li, V. C. Tung, P. Amsalem, N. Koch, *Commun. Phys.* **2019**, 2, 109.
- [37] S. Park, H. Wang, T. Schultz, D. Shin, R. Ovsyannikov, M. Zacharias, D. Maksimov, M. Meissner, Y. Hasegawa, T. Yamaguchi, S. Kera, A. Aljarb, M. Hakami, L.-J. Li, V. Tung, P. Amsalem, M. Rossi, N. Koch, S. Park, H. Wang, M. Zacharias, D. Maksimov, M. Rossi, T. Schultz, D. Shin, P. Amsalem, N. Koch, *Adv. Mater.* **2021**, 33, 2008677.
- [38] S. Park, T. Schultz, D. Shin, N. Mutz, A. Aljarb, H. S. Kang, C. H. Lee, L. J. Li, X. Xu, V. Tung, E. J. W. List-Kratochvil, S. Blumstengel, P. Amsalem, N. Koch, *ACS Nano* **2021**, 15, 14794.
- [39] S. Mouri, Y. Miyauchi, K. Matsuda, *Nano Lett.* **2013**, 13, 5944.
- [40] F. Zhang, A. Kahn, F. Zhang, A. Kahn, *Adv. Funct. Mater.* **2018**, 28, 1703780.
- [41] S. Park, T. Schultz, A. Han, A. Aljarb, X. Xu, P. Beyer, A. Opitz, R. Ovsyannikov, L.-J. Li, M. Meissner, T. Yamaguchi, S. Kera, P. Amsalem, N. Koch, *Commun. Phys.* **2019**, 2, 68.
- [42] J. Ma, P. Amsalem, T. Schultz, D. Shin, X. Xu, N. Koch, *Adv. Electron. Mater.* **2021**, 7, 2100425.
- [43] C.-H. Chang, X. Fan, S.-H. Lin, J.-L. Kuo, *Phys. Rev. B* **2013**, 88, 195420.
- [44] F. Caruso, P. Amsalem, J. Ma, A. Aljarb, T. Schultz, M. Zacharias, V. Tung, N. Koch, C. Draxl, *Phys. Rev. B* **2021**, 103, 205152.
- [45] S. Winkler, P. Amsalem, J. Frisch M. Oehzelt, G. Heimel, N. Koch, *Mater. Horiz.* **2015**, 2, 427.
- [46] J. B. Torrance, J. J. Mayerle, K. Bechgaard, B. D. Silverman, Y. Tomkiewicz, *Phys. Rev. B* **1980**, 22, 4960.
- [47] P. Beyer, D. Pham, C. Peter, N. Koch, E. Meister, W. Brütting, L. Grubert, S. Hecht, D. Nabok, C. Cocchi, C. Draxl, A. Opitz, *Chem. Mater.* **2019**, 31, 1237.
- [48] B. Schuler, D. Y. Qiu, S. Refaely-Abramson, C. Kastl, C. T. Chen, S. Barja, R. J. Koch, D. F. Ogletree, S. Aloni, A. M. Schwartzberg, J. B. Neaton, S. G. Louie, A. Weber-Bargioni, *Phys. Rev. Lett.* **2019**, 123, 076801.
- [49] K. F. Mak, K. He, C. Lee, G. H. Lee, J. Hone, T. F. Heinz, J. Shan, *Nat. Mater.* **2012**, 12, 207.
- [50] E. Tapavicza, F. Furche, D. Sundholm, *J. Chem. Theory Comput.* **2016**, 12, 5058.
- [51] N. J. Stanton, R. Ihly, B. Norton-Baker, A. J. Ferguson, J. L. Blackburn, *Appl. Phys. Lett.* **2021**, 119, 23302.
- [52] H. Zeng, P. Durand, S. Guchait, L. Herrmann, C. Kiefer, N. Leclerc, M. Brinkmann, *J. Mater. Chem. C Mater.* **2022**, 10, 15883.
- [53] S. Park, N. Mutz, T. Schultz, S. Blumstengel, A. Han, A. Aljarb, L. J. Li, E. J. W. List-Kratochvil, P. Amsalem, N. Koch, *2D Mater.* **2018**, 5, 025003.