

Exciton and Excited-State Charge Transfer at 2D van der Waals Interfaces

Nicolas Zorn Morales, Daniel Steffen Rühl, Emil List-Kratochvil, and Sylke Blumstengel*

Combining materials with diverse properties into two-dimensional (2D) van der Waals heterostructures lies at the heart of electronic, optoelectronic, and photonic applications. Prerequisite is a significant degree of electronic or photonic coupling of the constituents across the heterointerface. Understanding and controlling these interactions is mandatory to achieve the desired functionality. This review focuses on the charge and energy transfer processes and their dynamics in a specific class of van der Waals heterostructures, namely such composed of semiconducting transition metal dichalcogenides and conjugated organic molecules. With the help of prototypical material combinations, the importance of a precise knowledge of the interfacial electronic structure is demonstrated as it governs the excited-state dynamics. This review aims at providing basic design guidelines to achieve functional 2D organic/inorganic van der Waals heterostructures with final properties that can be designed by careful selection of the organic component.

epitaxy opens up a wide field of study to create heterostructures that display novel physical phenomena and enable unique functionality.^[2,9] Of fundamental importance are interlayer interactions that give rise to electronic,^[10–13] optical,^[14,15] and magnetic^[7,16] properties of vdWH which can be qualitatively different from those of their isolated components. An example is the transition from a direct to an indirect bandgap in group VI TMDCs when changing the number of layers.^[17,18] Further degree of freedom can be added when combining inorganic layered materials with organic molecules that can be costume designed with predictable properties.^[19–25]

This review focuses on the possibilities offered by interfacing semiconducting group VI TMDCs with conjugated organic molecules. In the monolayer (1L) regime,

these TMDCs have a direct bandgap.^[17,18] Due to their 2D nature and the reduced dielectric screening, Coulombically bound states, i.e., excitons, dominate the optical response of MoS₂, MoSe₂, WS₂, WSe₂ monolayers up to room temperature.^[26–30] They are responsible for the large light–matter interaction cross section. Though the exciton binding energies are comparable to that of organic compound's Frenkel excitons,^[31] the exciton wave functions are of Wannier–Mott-type due to the crystalline nature of the materials.^[28] The favorable optical properties combine with fairly high charge carrier mobilities up to a few hundred cm² V^{−1} s^{−1} and the feasibility of p- and n-doping.^[4,32–34] These properties combined make semiconducting TMDCs attractive as ultrathin, flexible, and semitransparent platforms for photon harvesting, sensing, and generation, and possibly also for nonlinear optical applications.^[5,6,30] Further enhancement of the performance is expected by hybridization with conjugated organic molecules. For example, although being direct bandgap semiconductors, 1L-TMDCs generally suffer from comparably low photoluminescence (PL) yield at room temperature due to defect-mediated nonradiative recombination.^[35] On the other hand, conjugated organic molecules are known for their high PL quantum yield which can reach 100%. Therefore, the combination of 1L-TMDC with organic molecules could be used to enhance the light output. Furthermore, despite the large light–matter interaction cross section, the absorption of normal incidence light at the excitonic peaks in the atomically thin TMDCs is naturally low (≈5%). Again, an approach to overcome this problem is the combination of 1L-TMDCs with conjugated organic molecules which also feature strong light–matter coupling. If properly designed, molecular layers can enhance and

1. Introduction

The seminal work by Geim & Grigorieva^[1] on van der Waals heterostructures (vdWH) has ignited an immense research interest in a wide range of two-dimensional (2D)-layered materials including graphene, transition metal dichalcogenides (TMDCs), hexagonal BN, 2D perovskites with properties spanning the range from insulator, via semiconductor with tunable bandgap, to conductor and superconductor.^[2–9] The feasibility of assembling materials with such diverse properties without the restraints imposed by lattice constant matching as in classical

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spectrally tune light absorption and emission of such heterostructures.^[23,36–42] Prerequisite is that the excitation energy deposited in the organic layer is transferred to the TMDC and this requires either nonradiative resonance energy transfer (RET)^[11] or excited-state charge transfer (CT) across the heterointerface. The occurrence of these transfer processes at several organic/TMDC interfaces has been experimentally demonstrated,^[25,37,40,42–46] theoretically treated,^[47] and its dynamics studied.^[48,49] In particular, excited-state CT between the organic component and the TMDCs^[37,38,50–52] as well as RET from organic molecules to TMDCs^[39,40,42] have been utilized to enhance the photosensitivity and to tune the spectral range in nanoscale photodetecting devices.^[23,53]

Previous studies of heterostructures comprises conjugated organic molecules and quantum wells made of 3D semiconductor like GaN and ZnO have identified several requirements to achieve the desired function of the molecular layer.^[54–60] RET requires spectral overlap between the absorption spectrum of the acceptor and the PL spectrum of the donor (Figure 1a). The interactions that mediate RET, i.e., coulomb (Förster-type) or exchange (Dexter-type) interaction, are short ranged (typically < 5 nm). Therefore, the molecules must assemble in homogeneous thin films close to the TMDC surface to achieve high RET efficiencies. The direction and efficiency of CT, on the other hand, are governed by the energy-level alignment at the heterointerface. Due to the weak interlayer coupling at the organic/inorganic interface, the electronic states are approximately localized within the individual layers, and the band alignment results from the band edge energies of the constituent layers. Possible configurations are shown in Figure 1b,c. When the lowest occupied energy levels of electrons and holes reside in the same layer, a straddling type-I band alignment is formed (Figure 1b). When the lowest occupied energy level of electrons resides in one layer and that of holes in the other layer, then a staggered type-II band alignment is obtained (Figure 1c). The possible CT processes after optical excitation or charge carrier injection are indicated by the arrows. Charge separation, for example, requires a type-II energy-level alignment with sufficiently large energy offsets between the frontier molecular orbital levels and the valence and conduction band edges of the 2D semiconductor to drive efficient exciton dissociation. On the other

hand, when aiming at light-emitting applications, a type-I energy-level alignment is needed to avoid exciton dissociation and concomitant luminescence quenching. Furthermore, in such configuration, excitation energy can be transferred not only via excitonic coupling (dipole–dipole interaction) but also by simultaneous injection of electrons and holes into the lower bandgap material. Unfortunately, the prediction of the energy-level alignment based on electronic structure data of the individual components is highly problematic because the energy gap as well ground-state charge CT of 1L-TMDCs are strongly influenced by the supporting substrates.^[61,62] To obtain the intrinsic properties of a given TMDC/organic interface, a pertinent study of the material combination of interest on the respective supporting substrate has to be conducted.

This review is intended to devise reliable design strategies for optimized opto-electronic functionality of organic/TMDC heterointerfaces. This is done by focusing on two widely studied prototypical material combinations serving as benchmark examples, namely on perylenetetracarboxylic dianhydride (PTCDA) and phthalocyanines (Pc) in combination with 1L-TMDCs.

Early studies on the assembly and electronic structures of PTCDA^[63–66] and Pc^[67,68] on bulk TMDCs date back a long time before the advent of 2D materials. The crystalline van der Waals surface of TMDCs without dangling bonds was considered an attractive underlay to produce well-ordered molecular assemblies and this had motivated these studies. Here, the focus is on opto-electronic applications and therefore we focus on the combination with TMDCs in the monolayer regime and consider in particular applications of the heterostructures for photodetectors.

The review is organized as follows. In the first part, we consider heterostructures with a type-II energy-level alignment. In this category fall Pc/1L-MoS₂ heterostructures.^[38,41,43–45,50,52,69–75] This material combination has been mostly investigated with respect to applications in photodetecting devices. The second part is dedicated to the PTCDA/1L-TMDC interface.^[39,42,51,76–81] Here, the energy-level alignment is debated and therefore this material combination represents a case study for the importance of a precise knowledge of the interfacial electronic structure in order to understand the excited-state dynamics. Combination with PTCDA has

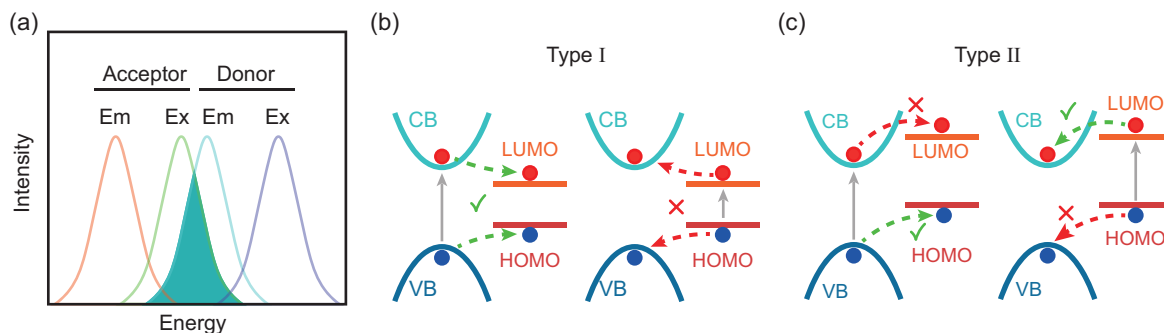


Figure 1. a) Spectral overlap condition for RET. The RET rate constant is proportional to the spectral overlap integral between the PL spectrum of the donor and the absorption spectrum of the acceptor (turquoise shaded area). b) Straddling type-I energy-level alignment. Simultaneous transfer of electrons and holes is possible from the higher to the lower bandgap material. c) Staggered type-II energy-level alignment. The possible CT routes are indicated. HOMO: highest occupied molecular orbital, LUMO, lowest unoccupied molecular orbital; VB, valence band; and CB, conduction band of the TMDC.

been proposed to enhance the photoresponse as well as the PL yield of 1L-MoS₂.

2. Pc/MoS₂ Heterostructures: Excited-State Charge Transfer

2.1. Pc/MoS₂-Based Photodetectors

We start the discussion with the presentation of an application where functionalization with organic molecules has been shown already to improve the performance of 1L-TMDCs, namely that of photodetecting devices. In its simplest form, a photodetector is a photoconductor, where the absorption of photons increases the charge carrier density and thus the conductivity of the material. Photodetectors based on TMDCs and in particular on 1L-MoS₂ have been widely reported in the literature.^[82–84] Very high responsivities ($R = 10^3 \text{ A W}^{-1}$) in the visible spectral range are achieved for 1L-MoS₂ photoconductors,^[85] which are attributed to a large photoconductive gain or, in other terms, to persistent photoconductivity.^[86–88] The gain is defined as $G = \tau/t$, where τ is the lifetime of the trapped charge carriers (holes in the case of MoS₂)^[87] and t is the transit time of the opposite carriers (i.e., electrons). The gain arises when one of the charge carriers recirculates many times before it recombines with his opposite counterpart. Unfortunately, a large photoconductive gain is naturally accompanied by a slow temporal response, which is governed by the trapped carriers' lifetime τ . Defect engineering has been used to enhance the dynamic response, however, mostly at the cost of the photosensitivity since the trap induced gain mechanism is reduced.^[89] The combination of MoS₂ or TMDCs in general with organic materials can be advantageously twofold: first, it could boost the response in spectral regions where the TMDC does not or only weakly absorb,^[38,90] and second it could help to speed up the response of the photodetectors^[50,70,73] while maintaining a high responsivity.^[91]

Among the most studied material combinations are 1L-MoS₂ in conjunction with Pc molecules, including the hydrogenated

H₂Pc as well as the metal derivatives Me-Pc. These molecules are widely used in organic photovoltaic devices due to their excellent chemical stability. **Figure 2** presents data obtained for a photodetector based on a H₂Pc/1L-MoS₂ heterostructure.^[38] The design of the two-point device is depicted in Figure 2a. The absorption spectra of the two components are depicted in Figure 2b. The absorption spectrum of the H₂Pc layer comprises the Soret band >3 eV and the Q-band with two main features at 1.94 and 1.78 eV.^[92,93] The 1L-MoS₂ absorption spectrum features the A, B, and C excitonic transitions at 1.91, 2.05, and 2.90 eV, respectively. Photocurrent action spectra of the H₂Pc/1L-MoS₂ and a reference 1L-MoS₂ device are recorded under an external bias of the structure employing a modulation technique that guarantees that any residual contribution of persistent photoconductivity^[86–88] is removed from the spectra (Figure 2b). Whereas the photoresponse of the reference 1L-MoS₂ device directly follows the absorption spectrum of 1L-MoS₂, additional features due to a photocurrent contribution arising from the absorption of photons in the H₂Pc layer are clearly visible. One explanation could be the formation of a second photoconducting channel through the H₂Pc layer of the device. However, this is ruled out since no photocurrent is detectable in H₂Pc-only devices.^[38] Considering the discontinuous film morphology (Figure 2c), it is highly unlikely that conductive paths can form in the organic film. Therefore, the excitation energy deposited in the organic layer must be transferred to the 1L-MoS₂ to create additional carriers there and to increase the conductivity of the 1L-MoS₂. Most remarkably, a photocurrent is even produced in spectral regions where the TMDC does not absorb. Thus, the spectral sensitivity range of the 1L-MoS₂-based photodetector expanded to longer wavelengths. In a more detailed follow-up study presented in this issue,^[91] the photoresponse dynamics is investigated by intensity-modulated photocurrent spectroscopy with steady-state background illumination. It is found that the deposition of the H₂Pc layer speeds up the photoresponse as compared to a reference 1L-MoS₂ photodetector by almost two orders of magnitude

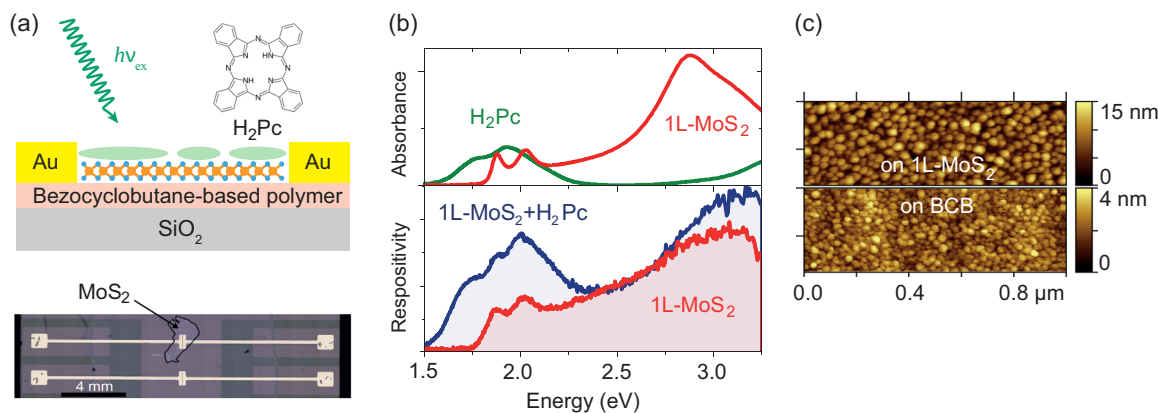


Figure 2. a) Upper panel: Schematic depiction of a H₂Pc/1L-MoS₂ photodetector. The nominal thickness of the vapor-deposited molecular layer is 3 nm. Lower panel: Photograph of the device. The channel length is 30 μm and the channel width 1 mm. b) Upper panel: Absorbance of 1L-MoS₂ and of the 3 nm-thick H₂Pc layer. Lower panel: Photoresponse of the heterostructure (blue) and the pristine 1L-MoS₂ (red) device. The spectra are normalized at the spectral position where H₂Pc does not absorb, i.e., between 2.5 and 2.55 eV. c) AFM images of the morphology of the nominally 3 nm-thick H₂Pc film on 1L-MoS₂ and on the benzocyclobutene (BCB) underlay. The molecular coverage is ≈85% of the surface. Adapted with permission.^[38] Copyright 2020, American Chemical Society.

without deteriorating its responsivity. It is shown that the improved response speed of the heterostructure arises mostly from a faster detrapping of holes in presence of the molecules, while the additional absorption of photons in the H₂Pc layer contributes to photocarrier generation, resulting in an enlarged responsivity of the heterostructure. The underlying energy-level alignment and excited-state dynamic leading to this improved performance are discussed in the next section.

2.2. Energy-Level Alignment at Pc/MoS₂ Interfaces

A prerequisite for the understanding of the CT processes at heterointerfaces is the precise knowledge of the energy positions of the occupied and unoccupied levels of the constituents when brought into contact. As pointed out earlier, the bandgap, the ionization potential (IP), as well as the electron affinity (EA) of TMDCs depends on the dielectric environment as well as on the workfunction of the underlay. Therefore, the choice of the substrate has to be considered,^[31,61] since it will influence the energy-level alignment at the heterointerface. In the following, we discuss heterostructures on SiO₂, as it is typically used as a gate dielectric in hybrid photodiodes and phototransistors.^[69,70] Figure 3a shows angle-resolved direct (ARPES) and inverse (ARIPES) photoemission spectra of the pristine and H₂Pc covered 1L-MoS₂. The spectra of the pristine surface are recorded at the K point of the Brillouin zone to properly determine the energetic positions of the valence band maximum (VBM) as well as the conduction band minimum (CBM) of 1L-MoS₂. The spectra of the heterointerface are recorded the Γ -point since

dispersion in the H₂Pc nanocrystalline film is negligible. The level onsets of the valence features are found at binding energies of 1.8 eV for the 1L-MoS₂ VBM and 0.9 eV for the H₂Pc HOMO below the Fermi level, yielding an energy offset between the occupied levels of 0.9 eV. The positions of the unoccupied levels are derived from IPES. Here, the level onsets are found at 0.3 eV for the 1L-MoS₂ CBM and at 1.3 eV for the H₂Pc LUMO above the Fermi level yielding an energy offset of 1 eV. Since the energy offsets between the occupied and unoccupied levels have the same sign, a type-II energy-level alignment is obtained (Figure 3b) and the prerequisite for excited-state CT is fulfilled. On the other hand, ground-state CT which has been invoked at the Zn-Pc/H₂Pc interface^[44,73] is ruled out at the 1L-MoS₂/H₂Pc since no shift in the valence and core-level features and only an insignificant change in the work function upon the deposition of the molecules is observed.^[38]

2.3. Excited-State Dynamics at Pc/MoS₂ Interfaces

The transfer mechanism and an estimate of the efficiency of the CT are obtained by steady state and time-resolved PL measurements. Figure 3c compares absorption and PL spectra of the subsystems from which it is immediately clear that RET from H₂Pc to 1L-MoS₂ is not possible. Though the transport gap of H₂Pc is larger than that of 1L-MoS₂, its optical gap is smaller due to the larger exciton binding energy of the organic material. The opposite direction of RET, namely from 1L-MoS₂ to H₂Pc, is possible, and—though not expected on a first glance—might also contribute to free carrier generation 1L-MoS₂ as discussed later. The leading

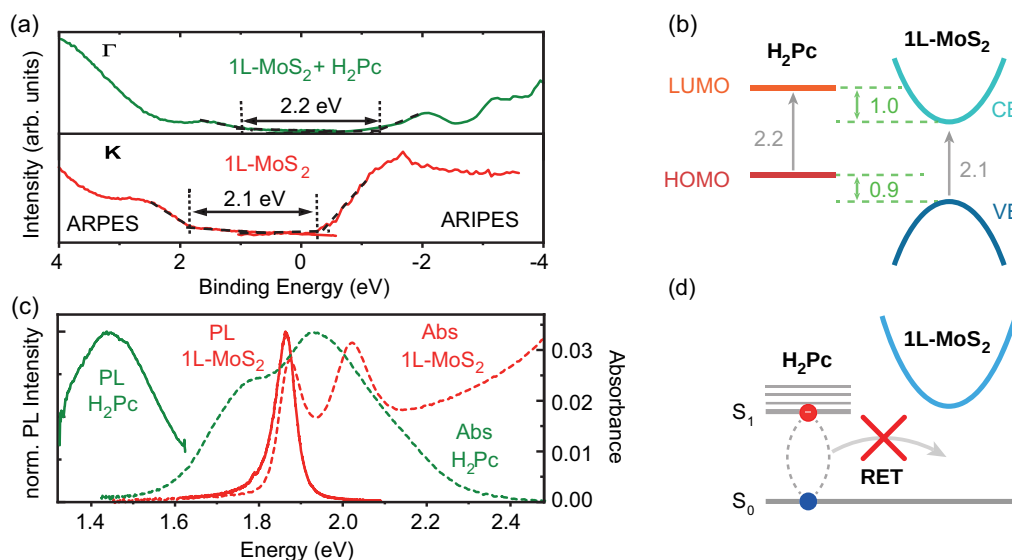


Figure 3. a) Occupied (ARPES) and unoccupied (ARIPES) levels at the H₂Pc (2 nm)/1L-MoS₂ interface (green) and of the pristine 1L-MoS₂ (red). The HOMO and LUMO as well as VBM and CBM positions are indicated by dashed lines. To obtain a more accurate CBM onset, the IPES spectra are deconvoluted. The error of the deduced binding energies is ± 50 meV. b) Energy-level diagram of the 1L-MoS₂/H₂Pc interface derived from UPS and IPES showing a type-II alignment facilitating excited-state CT. c) Absorbance and PL spectra of reference samples of a 3 nm-thick H₂Pc film (green) and 1L-MoS₂ (red) on SiO₂ substrates. The relevant spectra for the calculation of the spectral overlap integral are plotted as thick lines. Apparently, there is no spectral overlap between the PL of H₂Pc and the absorption 1L-MoS₂ (thick lines). d) Energy-level diagram of the 1L-MoS₂/H₂Pc interface derived from UPS and IPES showing a type-II alignment facilitating excited-state CT. e) Since the optical gap of 1L-MoS₂ is larger than that of H₂Pc, RET from H₂Pc to 1L-MoS₂ cannot contribute to the enhanced photoresponsivity of the heterostructure. Adapted with permission.^[38] Copyright 2020, American Chemical Society.

mechanism causing the enhancement of the photoresponse of 1L-MoS₂ is, however, excited-state CT. At photon energies $E_{ph} > 1.8$ eV, both components are excited (see **Figure 4a**), and thus electron transfer from the H₂Pc's LUMO to the conduction band of 1L-MoS₂ as well as hole transfer from the valence band of 1L-MoS₂ to the HOMO of the molecule can contribute. At $E_{ph} < 1.8$ eV, only H₂Pc is excited, and thus, only electron transfer from the H₂Pc's LUMO to the conduction band of 1L-MoS₂ is possible. The quenching rate of H₂Pc excitons due to charge separation at the heterointerface is obtained by time-resolved PL measurements. **Figure 4b** compares the PL transients of H₂Pc obtained for a reference film deposited on SiO₂ with that of the H₂Pc film on 1L-MoS₂. A pronounced shortening of the PL decay of the latter is observed. Since the H₂Pc layer thickness ($d = 1.2$ nm) in the present experiment is much smaller than the exciton diffusion length in the nanocrystalline film (5 nm),^[94] the efficiency of H₂Pc exciton dissociation η_{diss} is equal to the PL quenching efficiency $\eta_{diss} = (I_0 - I_h)/I_0$, where I_0 and I_h are the H₂Pc PL yields of the reference sample and the heterostructure, respectively. Integrating the normalized PL transients after deconvolution with the instrument response function yields $\eta_{diss} \approx 0.85$. The dynamics of the transfer processes is too fast (sub-ps time domain) to be fully captured by the time-correlated single photon counting technique employed to measure the PL decay. Therefore, the excited-state dynamics is typically studied by transient absorption spectroscopy (TAS)^[71] and time-resolved two photon photoemission spectroscopy (tr-TPPE).^[43–45,95] According to TAS, the time constant of electron transfer after excitation of H₂Pc is < 320 fs.^[45] Photoexcitation of 1L-MoS₂, on the other hand, may result in

1) hole transfer to the molecule's HOMO leaving an electron in the 1L-MoS₂ conduction band and 2) energy transfer to H₂Pc and subsequent electron transfer to the conduction band of 1L-MoS₂. Since TAS cannot entangle the two pathways, only a common time constant of ≈ 800 ps of the two pathways can be given.^[45] It should be noted that pathway (2) has been observed also at other organic/inorganic semiconductor heterointerfaces.^[57,58] Exciton dissociation at the heterointerface is the first step in the generation process of free charge carriers. As an intermediate state, Coulombically bound electron-hole pairs are formed. These so-called charge-transfer states have been observed at various organic/inorganic semiconductor interfaces^[59,96] and signatures in PL spectra have been invoked also at organic/TMDC interfaces.^[97,98] Only when the charge-transfer state dissociates, free charge carriers are formed and a photoconductive response is generated. Since excited-state CT occurs on a very fast time scale in the considered system, the limiting factor for an efficient free carrier generation is interfacial carrier recombination. According to TAS, the time constants for CT are very similar for hydrogenated H₂Pc and the metal derivatives. However, the lifetime of the charge-separated state is found to be considerably longer for Me-Pc (up to 70 ns for Cu-Pc) than for hydrogenated H₂Pc (≈ 5 ns).^[45] This difference is ascribed to a different stacking of the molecules on the MoS₂ surface: While H₂Pc assumes a mixed edge-on and face-on orientation on MoS₂, CuPc assembles in stacks flat-lying molecules. It is suggested that the longer lifetime of the charge-separated state observed at the CuPc/1L-MoS₂ interface is due to rapid hole migration away from the heterointerface which decreases the electron-hole Coulomb interaction and renders thus free carrier generation more efficient.

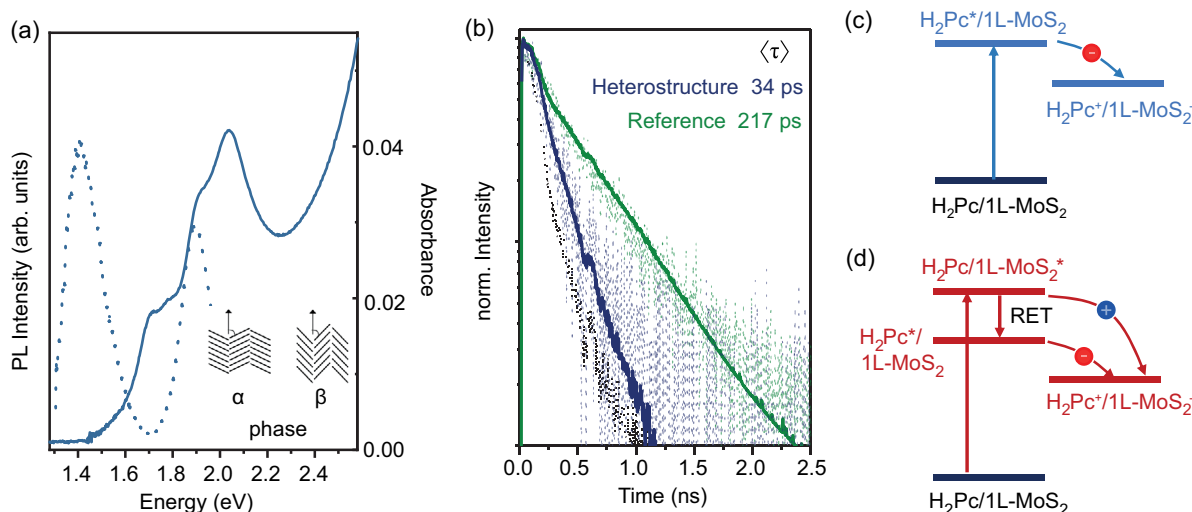


Figure 4. a) PL (dashed blue line) excited at 2.21 eV and the corresponding absorption spectrum (solid blue line) of the H₂Pc/1L-MoS₂ heterostructure on SiO₂. The H₂Pc layer thickness is $d_{H_2Pc} = 1.0$ nm. The inset shows the arrangement of the molecules in two crystal phases. b) PL transients of H₂Pc in a reference sample on SiO₂ with a layer thickness of $d_{H_2Pc} = 1.0$ nm (green dots) and in the H₂Pc/1L-MoS₂ heterostructure (blue dots). The excitation energy is 1.95 eV. The instrument response function (IRF) is shown as well (gray). The solid lines are fits to the decay curves obtained by convoluting a biexponential decay law with the IRF. The lifetimes given in the inset are time averages over these decay curves $\tau = \int t \cdot I(t) dt / \int I(t) dt$. c) Schemes of the transfer processes after selective photoexcitation of H₂Pc and of 1L-MoS₂. d) The asterisk denotes the excited state, plus/minus the charged state. Excitation of H₂Pc (c) is followed by electron transfer to the conduction band of 1L-MoS₂. Excited-state CT after photoexcitation 1L-MoS₂ (d) can proceed via two pathways: (1) hole transfer to the H₂Pc HOMO and (2) RET from 1L-MoS₂ to H₂Pc followed by electron transfer to the conduction band of 1L-MoS₂. Adapted with permission.^[38] Copyright 2020, American Chemical Society.

Besides the molecular arrangement, another important factor governing the efficiency of the charge separation and free carrier generation is the magnitude of the energy-level offsets as shown in a very recent work.^[99] Combined UPS and TAS experiments performed at a series of type-II molecule/1L-MoS₂ interfaces reveal that a larger energy-level offset causes a lower efficiency of hole transfer from photoexcited 1L-MoS₂ to the molecule's HOMO but also a longer lifetime of the CT state. Both observations are explained in the framework of Marcus' theory of electron transfer.^[100] The data suggests that photoinduced hole transfer from the TMDC VBM to the organic material's HOMO level is in the Marcus-inverted regime.^[100,101] It is concluded that the main decay pathway for photogenerated carriers in the considered systems is not direct electron-hole recombination across the heterointerface but back transfer of holes to the 1L-MoS₂. To achieve efficient charge separation, introduction of a thin LiF interlayer is suggested since such interlayer efficiently slows down interfacial carrier recombination while not affecting the free carrier formation. Further factors that are suggested to affect the charge separation and free carrier generation are discussed in the next section.

3. PTCDA/TMDC Heterostructures: Resonance Energy Transfer and Excited-State Charge Transfer

3.1. Prospective Applications of PTCDA/TMDC Heterointerfaces

Transition metal sulfides (1L-MoS₂, 1L-WSe₂) possess a rather large EA (≈ 4 eV for 1L-MoS₂ depending on the substrate).^[61] Therefore, typical organic hole transport materials (among them Pc) form type-II interfaces with the sulfides where the organic component serves as electron donor after photoexcitation. For molecules used as electron acceptors in organic electronics having also large EA (like PTCDA and its derivatives), the situation is debated, and therefore, controversy exists in the interpretation of experimental observations. In an early work, a PTCDA/1L-WSe₂ heterojunction is investigated under the premise of a type-II energy-level alignment where the organic component serves as electron acceptor.^[51] The energy-level diagram is constructed based on literature data of the isolated components. The quenching rate of the PL due to excited-state CT has been found to be about 5 times higher for 1L-WSe₂ excitons than for PTCDA excitons. The higher quenching efficiency of TMDC excitons is ascribed to the confinement of the excitons within the 2D semiconductor plane, while the PTCDA excitons may escape from the interface without quenching in the 10 nm thick layer. RET is not considered since the spectral overlap between the molecules PL and the 1L-WSe₂ absorbance is small. A photodiode made of the PTCDA/1L-WSe₂ heterojunction achieves a peak external quantum efficiency of $\approx 1.8\%$.^[51] RET is investigated in a heterostructure of PTCDA and 1L-MoSe₂.^[39] Here, PTCDA serves as donor and 1L-WSe₂ as acceptor. Replacing the sulfur with selenium decreases the optical gap of the TMDC resulting in spectral overlap between the PTCDA's PL with the B excitonic absorption of 1L-MoSe₂. From steady state and time-resolved PL measurements, an RET efficiency of 30% is inferred. The advantage of the flat-on adsorption of PTCDA on TMDC surfaces^[63,102] for

RET mediated via dipole-dipole interaction is emphasized. Since the transition dipole moment of the molecules and the TMDC are lying in the plane of the molecule and the monolayer, respectively, and are thus parallel to each other the interaction strength is maximized. Application of such heterostructure for high efficiency energy harvesting systems that cover a wide spectral range is suggested. In another series of works, the PL properties of PTCDA/1L-MoS₂ heterostructures on Si/SiO₂ are investigated and a giant enhancement of both the PTCDA as well as the 1L-MoS₂ PL is reported.^[77,80] The explanation is based on the assumption of a type-II energy-level alignment with PTCDA serving as electron acceptor. The energy offset between molecules HOMO level and the 1L-MoS₂ VBM of 0.5 eV is derived from separately determined values of the electron affinity and ionization energy of the individual materials and from theoretical modeling. This interpretation is surprising since type-II interfaces are typically associated with a strong quenching of the PL.^[37,38,48,51] The ordered growth of the PTCDA layer on the crystalline van der Waals surface is invoked as an explanation of the PTCDA PL enhancement.^[63,102] The PL enhancement of MoS₂ is partly ascribed to a hybridization of the molecular orbitals with that of the TMDC and partly to electron transfer from the natively n-doped MoS₂ to PTCDA leading to a dedoping of the monolayer. The latter is concluded from a deconvolution of the overlapping PTCDA and 1L-MoS₂ PL signals from which an increase of the exciton to trion PL ratio is inferred in presence of the molecules. The PL enhancement is explained by the larger PL quantum yield of excitons as compared to trions.^[77,80] The excited-state dynamics at PTCDA/1L-MoS₂ interfaces in comparison to a series of other heterointerfaces (PTCDI/1L-MoS₂, PTCDI/1L-WSe₂, C60/1L-MoS₂, C60/1L-WSe₂) is studied by tr-TPPE.^[81] The substrate is SiO₂/Si. Based on the assumption of a type-II energy-level alignment with the molecular component as electron acceptor, it is suggested that the electron transfer rate from the photoexcited TMDC to organic molecules can be sensitive to the interfacial band offset and the bandwidth of the organic crystals LUMO. A large energy offset in combination with a small LUMO bandwidth (PTCDI/1L-WSe₂) leads to a decrease of the electron transfer rate by more than one order of magnitude (530 vs 20 fs at PTCDI/1L-MoS₂), while for molecules with large LUMO bandwidth (C60), the electron transfer rate is insensitive to the size of the energy offset. It is argued that a slow CT process might be out competed by other recombination processes in the TMDC and thus limit the performance of a resultant optoelectronic device.^[81] Finally, PTCDA/1L-MoS₂ on SiO₂/Si three-point devices have been suggested for use in neuromorphic computing.^[78] The explanation of the electric characteristics of that heterojunction is based on excited-state CT across the assumed type-II interface.

3.2. Energy-Level Alignment at the PTCDA/1L-MoS₂ Heterointerface

Since PTCDA/TMDC heterointerfaces are attractive for a wide range of applications, it is worthwhile to take a closer look at the energy-level alignment and its impact on the excited-state dynamics of one prototypical example. To that end, a PTCDA/1L-MoS₂ heterointerface on sapphire substrate is

considered in more detail.^[42] Photoemission spectroscopy at PTCDA/bulk MoS₂ interfaces has been performed in very early works.^[64,65] However, the results cannot be transferred to the present heterostructure since thinning down TMDCs from multi- to monolayer results in an indirect-to-direct gap transition and an concomitant increase of the bandgap^[103] and, therefore, the energy-level alignment is expected to change as well. The energy-level alignment at the PTCDA/1L-MoS₂ interface derived from ARPES and ARIPEs measurements is depicted in **Figure 5a**.^[42] The small vacuum level shift due to a surface electron push-back effect is in analogy to what has been observed for the deposition of molecules onto various inert metal oxide surfaces.^[104] Neither core level nor valence photoelectron spectra yield any indication for a hybridization of the PTCDA orbitals with those of MoS₂ or signs of interfacial charge transfer as invoked in some other works.^[77,80] This points toward a van der Waals-type interaction at the interface which is also predicted by density functional theory.^[79] Remarkably, the PTCDA levels straddle those of 1L-MoS₂ in a type-I manner, yielding values for the energy offsets of the occupied and unoccupied levels of 270 and 170 meV, respectively. It should be noted that the low binding energy HOMO manifold onset is used to construct the energy-level diagram^[42] since it is the relevant energy for charge carrier transfer^[105,106] instead of the peak maximum of the HOMO photoemission feature, as sometimes found in literature. As mentioned earlier, the IP and the EA of 1L-TMDCs depend on the substrate work function and dielectric constant.^[61] In the examples discussed in the previous section, native SiO₂/Si is used as underlay. Here, ground-state charge transfer from the substrate leads to small decrease (100 ... 200 meV) of the IP and EA^[61] which should increase the offset of the occupied levels and lead to a nearly aligned 1L-MoS₂ CBM and PTCDA LUMO. On sapphire, the energy-level alignment is, however, clearly of type I and, as a consequence, the dissociation of optically excited bound

electron-hole pairs, i.e., excitons, and interfacial charge separation is energetically not favored.

3.3. RET at the PTCDA/1L-MoS₂ Heterointerface

At a type-I interface, the only excited-state transfer process possible after photoexcitation is the transfer of excitons via RET. In the present configuration, excitons from PTCDA could be transferred to 1L-MoS₂, and this process can explain an increase of the PL yield as well as of the photoresponse of 1L-MoS₂. The RET process is evaluated with three samples (**Figure 5b**): a pristine 1L-MoS₂, a hybrid sample (with 6 nm PTCDA), and a PTCDA reference sample (with 18 nm PTCDA). Organic crystals show often polymorphism. Furthermore, structure and morphology and with that the PL properties of thin PTCDA films are known to depend strongly on the deposition conditions and substrate.^[107,108] To disentangle the effects of the film morphology and of the interaction with the TMDC on the spectra and on the excited-state dynamics of the organic layer, the reference and hybrid samples that are compared must have the same thin film structure. The 18 nm-thick PTCDA film on 1L-MoS₂ is a suitable reference since the film morphology is the same as that of the hybrid sample, while the optical response is dominated by the contributions of molecular layers far from the interface. **Figure 6a** compares the optical spectra of the pristine 1L-MoS₂ and of the PTCDA reference. The PTCDA spectra are typical of that of polycrystalline films^[109,110] and shall not be discussed here. Important in the present context is that at room temperature, the prerequisite for efficient RET, namely spectral overlap is met. The A excitonic absorption of 1L-MoS₂ overlaps well with the PL spectrum of PTCDA. The Varshni shift of 1L-MoS₂ in the temperature range from 293 to 4.5 K is about 80 meV,^[111] while the PTCDA PL spectrum just narrows without displaying a significant spectral shift upon cooling (**Figure 6a**).

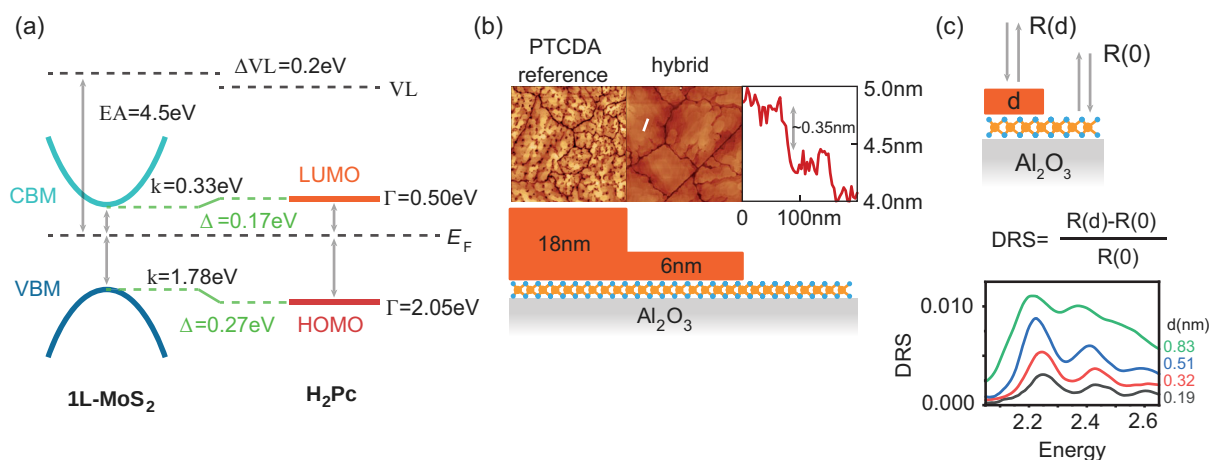


Figure 5. a) Schematic energy-level alignment at the PTCDA/1L-MoS₂ interface on sapphire substrate, as derived from ARPES and ARIPEs measurements.^[42] The values for the 1L-MoS₂ CBM and VBM are given at the K points of the Brillouin zone and that for PTCDA at the Γ point since dispersion in the organic material is negligible. b) Lower panel: Sample layout to study RET. Three regions are defined on a 1L-MoS₂ varying the PTCDA layer thickness d to yield a PTCDA reference sample ($d = 18 \text{ nm}$), a hybrid sample ($d = 6 \text{ nm}$) and a pristine 1L-MoS₂ sample ($d = 0 \text{ nm}$). Upper panel: AFM images of the morphology of the vapor deposited PTCDA films of the reference and hybrid sample. The scan size is $2 \times 2 \mu\text{m}^2$.^[42] The height scan is taken along the white line. The measured step height of $\approx 0.35 \text{ nm}$ corresponds closely to the spacing of the (102) plane of the PTCDA crystal suggesting a flat on adsorption of the molecules.^[102,125] c) Differential reflection spectra (DRS) recorded during the deposition of PTCDA on 1L-MoS₂. The monomer spectrum of PTCDA transforms into the aggregate spectrum when the second molecular layer starts to grow.^[109]

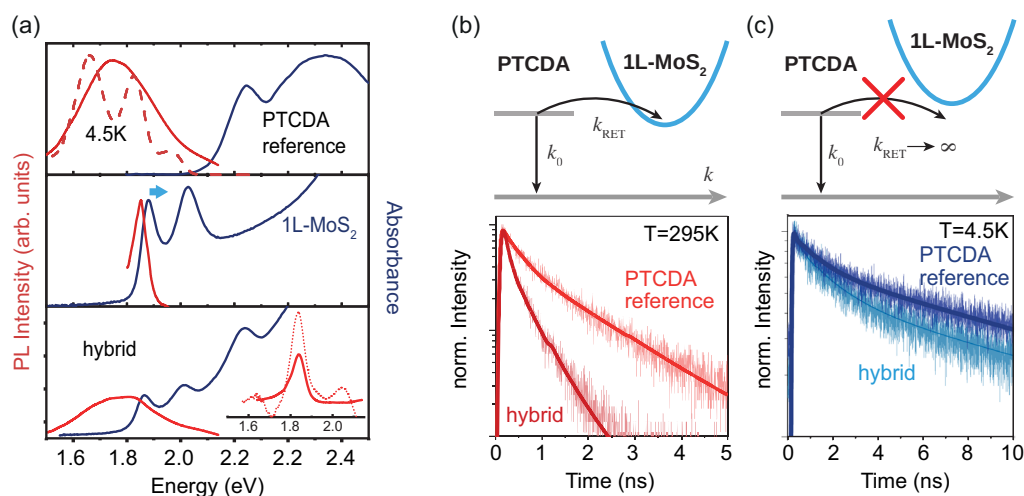


Figure 6. a) Upper panel: PL (red solid line) and absorbance (blue) spectra of the PTCDA reference film (18 nm) recorded at room temperature. The low-temperature PL at 4.5 K is shown as well (red dashed line). Center panel: PL (red) and absorbance (blue) spectra of the pristine 1L-MoS₂. The blue arrow indicates the magnitude of the Varshni shift when lowering the temperature from room temperature to 4.5 K. Lower panel: PL (red) and absorbance (blue) spectra of the PTCDA/1L-MoS₂ hybrid sample (6 nm PTCDA). The absorption spectrum is a superposition of the absorbances of the individual components. Inset: Comparison of the PL yield of 1L-MoS₂ of the pristine 1L-MoS₂ (solid line) and in the hybrid sample (dashed line). The latter is obtained by calculating the difference between the PL of the hybrid and that of the PTCDA reference scaled to the intensity of the hybrid PL at 1.65 eV, where 1L-MoS₂ does not emit to take the different layer thicknesses into account. The PL in all experiments is excited at 2.21 eV. b) PL transients of PTCDA in the PTCDA reference and the PTCDA/1L-MoS₂ hybrid sample recorded at 1.86 eV at room temperature (b) and c) at 4.5 K. The fits (thick solid lines) are obtained by convoluting biexponential decay laws with the IRF. The schemes above show the different decay channels of PTCDA molecules in the hybrid sample. τ_0 is the decay time of PTCDA due to radiative and nonradiative recombination, and τ_{RET} is the RET time constant. It becomes very long at low temperature due to the smallness of the spectral overlap integral. Adapted under the terms of the CC-BY license.^[42] Copyright 2021, The Authors. Published by Wiley-VCH GmbH.

Thus, by lowering the temperature, the system is tuned out of resonance, the spectral overlap vanishes, and thus RET is not expected to be efficient.

This is illustrated by time-resolved PL spectroscopy. Figure 6b, c compares PL transients of PTCDA in the reference and hybrid sample at room temperature and 4.5 K. While at room temperature, a strong shortening of the PTCDA PL is observed due to the additional decay channel opened up by RET, at low temperature, the observed change is small. The RET efficiency is given by $\eta_{\text{RET}} = (I_0 - I_h)/I_0$, where I_0 and I_h are the PTCDA PL yields of the reference and hybrid samples, respectively. Integrating the normalized PL transients after deconvolution with the IRF yields $\eta_{\text{RET}} \approx 0.85$ at room temperature and $\eta_{\text{RET}} \approx 0.30$ at 4.5 K. The observed drop of the RET efficiency with temperature provides further evidence that RET is the relevant transfer process that governs the PTCDA PL decay dynamics in the hybrid sample at room temperature. Most importantly, the excitation energy drained from PTCDA generates PL in 1L-MoS₂. This is shown in Figure 6a (lower panel) which compares the 1L-MoS₂ PL intensity of the pristine monolayer with that of the monolayer in the hybrid sample. Due to RET, the PL yield of 1L-MoS₂ in the hybrid is enhanced by a factor of ≈ 2 .

Like in the case of excited-state CT, the dynamics of RET is too fast to be resolved with the time-correlated single photon counting technique. To capture the RET kinetics, TAS of the heterostructure is performed (Figure 7).^[42] TAS of the individual components, namely of polycrystalline PTCDA films^[112] as well as of 1L-MoS₂,^[76,113–116] have been studied and analyzed, and the

reader is referred to the pertinent literature. Here, the focus shall be on the modifications of the excited-state kinetics due to the interaction of the two components to reveal the temporal evolution of the RET process. The decay of the PTCDA photoinduced absorption (PIA) signal (Figure 7b), reflecting the depopulation of the excited state, is nonexponential and shortens in the hybrid structure compared to the PTCDA reference. Due to the large exciton diffusion length in polycrystalline PTCDA films (20 ... 60 nm),^[112,117] RET from PTCDA to 1L-MoS₂ is not expected to be a single-step process but one assisted by diffusion and, furthermore, even in the PTCDA reference (18 nm PTCDA on ML-MoS₂), RET is not entirely negligible. RET can be mediated by dipole–dipole interaction, i.e., Förster transfer, and exchange interaction, i.e., Dexter transfer. The RET rate constant is in both cases distant dependent resulting in a distribution of RET rates and thus like diffusion in a nonexponential decay. The disentanglement of the individual contributions to the total energy transfer is not undertaken. However, an estimate of the characteristic RET time constant τ_{RET} of the molecules in direct contact with the 1L-MoS₂ is inferred from the initial short decay components of the hybrid structure $[(0.3 \pm 0.1) \text{ ps}]$ and the PTCDA reference $[(0.4 \pm 0.1) \text{ ps}]$ (see inset-table of Figure 7b). This time reflects the depopulation of the PTCDA excited state due to a single-step RET. It should be recalled that also the PTCDA reference sample contains 1L-MoS₂ and therefore, also in this sample there are molecules that decay on such short time scale due to the single-step RET to 1L-MoS₂ though the fraction of these molecules is much smaller than in the hybrid sample.

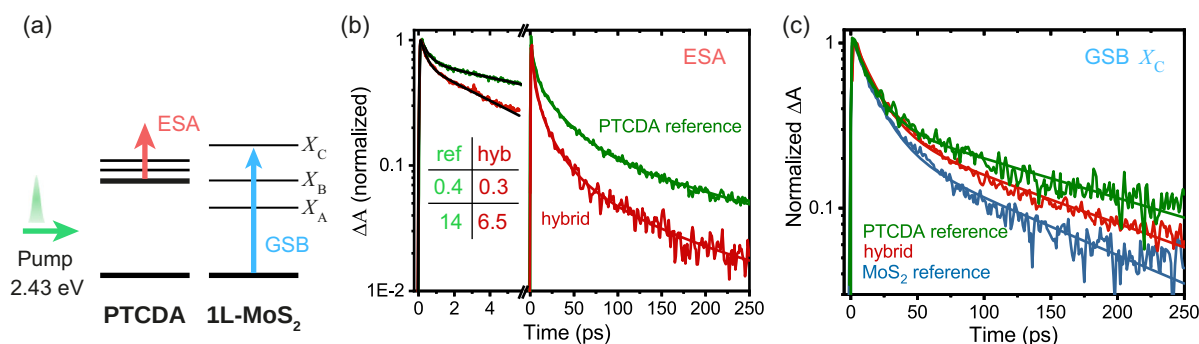


Figure 7. a) Schematic of the PTCDA/1L-MoS₂ heterojunctions (sample design like in Figure 5b) probed by TAS. After excitation with a pump pulse at 2.43 eV (70 ps pulse length), the sample is interrogated with a white probe pulse. The dynamics of the PIA signal in the spectral range of the PTCDA ESA (1.49–1.61 eV)^[125] and the PIB signal due to ground-state bleaching (GSB) in the spectral region of the C excitonic resonance of 1L-MoS₂ (2.75–2.95 eV) are studied. b) Kinetics of the ESA reflecting the depopulation of the PTCDA excited state. The table gives the time constants (in ps) for delay times between 0 and 5.7 ps. They are derived from fits of the decay transients in the respective time window which are obtained by convoluting biexponential decay laws with the IRF (solid lines). c) Kinetics of the PIB band dominated by the 1L-MoS₂ C excitonic resonance reflecting the supply of excitons from PTCDA via RET. The spectral regions of the A and B excitonic transitions overlap with the ESA of PTCDA and are therefore not analyzed. Adapted under the terms of the CC-BY license.^[42] Copyright 2021, The Authors. Published by Wiley-VCH GmbH.

Single-step RET to 1L-MoS₂ is apparently much faster than the radiative and nonradiative decay in PTCDA, since such short decay component is absent in PTCDA films on inert substrates at comparable excitation densities.^[112] This implies that the RET efficiency can reach 100% in sufficiently thin films. The supply of excitons to 1L-MoS₂ via RET occurring on different time scales (according to the distance of the molecules to the interface) is indicated by the slower decay kinetics of the PIB of the spectral region of the C excitonic transition in the hybrid and PTCDA reference sample.

The discussed examples show that due to the close proximity of donor and acceptor, RET from a molecular layer to TMDCs is highly efficient. It can be used to enhance the PL yield as well as the photoresponse of the atomically thin 2D material. The mechanism underlying RET has, however, not been studied yet. In heterostructures employing semiconductor quantum dots as donor, RET is discussed in the frame of the Förster theory. The distance d dependence of the RET rate contains information on the underlying physics of the transfer.^[118] However, $k_{\text{RET}} \approx d^m$ with different $m = 2.5\text{--}4$ have been found by introducing spacer layers between the quantum dots and the TMDC.^[119,120] Furthermore, the impact of the screening of the Coulomb interaction due to the dielectric environment has been emphasized.^[120,121] In case of molecular donors, both Dexter- as well as Förster-type transfer are expected to be active for molecules in close proximity to the TMDC. For the latter type, the dimensionality of the excitons in the two materials, namely delocalized Wannier-Mott excitons in the 2D plane of the TMDC and Frenkel excitons localized at the molecule (or delocalized in an aggregate comprising several molecules), is expected to result in peculiarities which are not captured by the classical Förster theory developed for molecular donor-acceptor systems.^[122] Previous experimental^[123] and theoretical^[124] studies of RET between Wannier-Mott excitons in inorganic semiconductor quantum well structures and Frenkel excitons in organic semiconductors have revealed a dependence of the dipole-dipole interaction matrix element V_{RET} on the wavevector k of the

Wannier-Mott exciton. For RET involving excitons delocalized in the quantum well plane, a dependence $V_{\text{RET}} \approx k \cdot e^{-kd}$ is predicted.^[124] In a very recent theoretical work on RET between TMDCs and organic molecules, a similar behavior has been found.^[47] It is proposed that mostly nonradiative excitons with $k > k_{\text{ph}}$, k_{ph} being the photon wave vector are involved in the RET process. Future more in-depth experimental studies are definitely needed.

4. Conclusion and Outlook

The discussed examples show that a combination with organic molecules can boost the performance of TMDC monolayers in optoelectronic devices. This involves the increase of the PL yield as well as the enhancement of the photoresponse and the tunability of the spectral sensitivity range as well as a modulation of the speed in photodetecting devices. Prerequisite is that the excitation energy deposited into the organic material is transferred to the TMDC. This requires efficient excited-state charge and/or energy transfer. The excited-state dynamics and with that the functionality of the interface is governed by the arrangement of the molecules on the TMDC surface and the energy-level alignment at the heterointerface. This regards the type of interface, straddling type I versus staggered type II as well as the magnitude of the energy offsets. The energy-level alignment depends sensitively on the workfunction of the substrate and dielectric environment of the heterointerface since both dielectric screening as well as ground-state CT modify EA and IP of the 2D semiconductor. Therefore, to achieve optimized optoelectronic function of the heterointerface, a precise knowledge of the energy-level alignment on a pertinent substrate/environment is mandatory as demonstrated at the PTCDA/TMDC example. This calls for future operando studies of the energy-level alignment and the excited-state dynamics employing relevant device geometries.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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- [1] A. K. Geim, I. V. Grigorieva, *Nature* **2013**, 499, 419.
- [2] K. S. Novoselov, A. Mishchenko, A. Carvalho, A. H. Castro Neto, *Science* **2016**, 353, aac9439.
- [3] M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, H. Zhang, *Nat. Chem.* **2013**, 5, 263.
- [4] H. Schmidt, F. Giustino, G. Eda, *Chem. Soc. Rev.* **2015**, 44, 7715.
- [5] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano, *Nat. Nanotechnol.* **2012**, 7, 699.
- [6] M. Ye, D. Zhang, Y. K. Yap, *Electronics* **2017**, 6, 43.
- [7] R. Beiranvand, H. Hamzehpour, *J. Appl. Phys.* **2017**, 121, 063903.
- [8] P. Miró, M. Audiffred, T. Heine, *Chem. Soc. Rev.* **2014**, 43, 6537.
- [9] Y. Liu, N. O. Weiss, X. Duan, H.-C. Cheng, Y. Huang, X. Duan, *Nat. Rev. Mater.* **2016**, 1, 16042.
- [10] L. A. Ponomarenko, R. V. Gorbachev, G. L. Yu, D. C. Elias, R. Jalil, A. A. Patel, A. Mishchenko, A. S. Mayorov, C. R. Woods, J. R. Wallbank, M. Mucha-Kruczynski, B. A. Piot, M. Potemski, I. V. Grigorieva, K. S. Novoselov, F. Guinea, V. I. Fal'ko, A. K. Geim, *Nature* **2013**, 497, 594.
- [11] R. V. Gorbachev, J. C. W. Song, G. L. Yu, A. V. Kretinin, F. Withers, Y. Cao, A. Mishchenko, I. V. Grigorieva, K. S. Novoselov, L. S. Levitov, A. K. Geim, *Science* **2014**, 346, 448.
- [12] B. Hunt, J. D. Sanchez-Yamagishi, A. F. Young, M. Yankowitz, B. J. Leroy, K. Watanabe, T. Taniguchi, P. Moon, M. Koshino, P. Jarillo-Herrero, R. C. Ashoori, *Science* **2013**, 340, 1427.
- [13] J. C. W. Song, N. M. Gabor, *Nat. Nanotechnol.* **2018**, 13, 986.
- [14] K. L. Seyler, P. Rivera, H. Yu, N. P. Wilson, E. L. Ray, D. G. Mandrus, J. Yan, W. Yao, X. Xu, *Nature* **2019**, 567, 66.
- [15] K. Tran, G. Moody, F. Wu, X. Lu, J. Choi, K. Kim, A. Rai, D. A. Sanchez, J. Quan, A. Singh, J. Embley, A. Zepeda, M. Campbell, T. Autry, T. Taniguchi, K. Watanabe, N. Lu, S. K. Banerjee, K. L. Silverman, S. Kim, E. Tutuc, L. Yang, A. H. Macdonald, X. Li, *Nature* **2019**, 567, 71.
- [16] Z. Wang, D.-K. Ki, H. Chen, H. Berger, A. H. Macdonald, A. F. Morpurgo, *Nat. Commun.* **2015**, 6, 8339.
- [17] K. F. Mak, C. Lee, J. Hone, J. Shan, T. F. Heinz, *Phys. Rev. Lett.* **2010**, 105, 136805.
- [18] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, F. Wang, *Nano Lett.* **2010**, 10, 1271.
- [19] K. Cho, J. Pak, S. Chung, T. Lee, *ACS Nano* **2019**, 13, 9713.
- [20] M. Gobbi, E. Orgiu, P. Samorì, *Adv. Mater.* **2018**, 30, 1706103.
- [21] H. Huang, Y. Huang, S. Wang, M. Zhu, H. Xie, L. Zhang, X. Zheng, Q. Xie, D. Niu, Y. Gao, *Crystals* **2016**, 6, 113.
- [22] Y. L. Huang, Y. J. Zheng, Z. Song, D. Chi, A. T. S. Wee, S. Y. Quek, *Chem. Soc. Rev.* **2018**, 47, 3241.
- [23] H. Li, Z. Dong, Y. Zhang, L. Li, Z. Wang, C. Wang, K. Zhang, H. Zhang, *2D Mater.* **2021**, 8, 012001.
- [24] K. Pei, T. Zhai, *Cell Rep. Phys. Sci.* **2020**, 1, 100166.
- [25] A. M. Steiner, F. Lissel, A. Fery, J. Lauth, M. Scheele, *Angew. Chem., Int. Ed.* **2021**, 60, 1152.
- [26] A. Chernikov, T. C. Berkelbach, H. M. Hill, A. Rigosi, Y. Li, B. Aslan, D. R. Reichman, M. S. Hybertsen, T. F. Heinz, *Phys. Rev. Lett.* **2014**, 113, 076802.
- [27] A. Ramasubramanian, *Phys. Rev. B* **2012**, 86, 115409.
- [28] G. Wang, A. Chernikov, M. M. Glazov, T. F. Heinz, X. Marie, T. Amand, B. Urbaszek, *Rev. Mod. Phys.* **2018**, 90, 021001.
- [29] K. F. Mak, J. Shan, *Nat. Photonics* **2016**, 10, 216.
- [30] T. Mueller, E. Malic, *npj 2D Mater. Appl.* **2018**, 2, 29.
- [31] 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.
- [32] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, *Nat. Nanotechnol.* **2011**, 6, 147.
- [33] L. Loh, Z. Zhang, M. Bosman, G. Eda, *Nano Res.* **2021**, 14, 1668.
- [34] M. Chhowalla, D. Jena, H. Zhang, *Nat. Rev. Mater.* **2016**, 1, 16052.
- [35] S. Roy, A. S. Sharbirin, Y. Lee, W. B. Kim, T. S. Kim, K. Cho, K. Kang, H. S. Jung, J. Kim, *Nanomaterials* **2020**, 10, 1032.
- [36] D. Jariwala, S. L. Howell, K.-S. Chen, J. Kang, V. K. Sangwan, S. A. Filippone, R. Turrissi, T. J. Marks, L. J. Lauhon, M. C. Hersam, *Nano Lett.* **2016**, 16, 497.
- [37] T. A. Shastri, I. Balla, H. Bergeron, S. H. Amsterdam, T. J. Marks, M. C. Hersam, *ACS Nano* **2016**, 10, 10573.
- [38] 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.
- [39] J. Gu, X. Liu, E.-C. Lin, Y.-H. Lee, S. R. Forrest, V. M. Menon, *ACS Photonics* **2018**, 5, 100.
- [40] C.-H. Cheng, Z. Li, A. Hambarde, P. B. Deotare, *ACS Appl. Mater. Interfaces* **2018**, 10, 39336.
- [41] E. P. Nguyen, B. J. Carey, C. J. Harrison, P. Atkin, K. J. Berean, E. Della Gaspera, J. Z. Ou, R. B. Kaner, K. Kalantar-Zadeh, T. Daeneke, *Nanoscale* **2016**, 8, 16276.
- [42] S. Park, N. Mutz, S. A. Kovalenko, T. Schultz, D. Shin, A. Aljarb, L.-J. Li, V. Tung, P. Amsalem, E. J. W. List-Kratochvil, J. Stähler, X. Xu, S. Blumstengel, N. Koch, *Adv. Sci.* **2021**, 8, 2100215.
- [43] T. R. Kafle, B. Kattel, S. D. Lane, T. Wang, H. Zhao, W.-L. Chan, *ACS Nano* **2017**, 11, 10184.
- [44] T. R. Kafle, B. Kattel, P. Yao, P. Zereski, H. Zhao, W.-L. Chan, *J. Am. Chem. Soc.* **2019**, 141, 11328.
- [45] S. Padgaonkar, S. H. Amsterdam, H. Bergeron, K. Su, T. J. Marks, M. C. Hersam, E. A. Weiss, *J. Phys. Chem. C* **2019**, 123, 13337.
- [46] S. Kwon, D. Y. Jeong, C. Hong, S. Oh, J. Song, S. H. Choi, K. K. Kim, S. Yoon, T. Choi, K.-J. Yee, J.-H. Kim, Y. You, D.-W. Kim, *Adv. Sci.* **2022**, 9, 2201875.
- [47] M. Katzer, S. Kovalchuk, K. Greben, K. I. Bolotin, M. Selig, A. Knorr, *Phys. Rev. B* **2023**, 107, 035304.
- [48] S. Bettis Homan, V. K. Sangwan, I. Balla, H. Bergeron, E. A. Weiss, M. C. Hersam, *Nano Lett.* **2017**, 17, 164.
- [49] C. Zhong, V. K. Sangwan, C. Wang, H. Bergeron, M. C. Hersam, E. A. Weiss, *J. Phys. Chem. Lett.* **2018**, 9, 2484.
- [50] J. Pak, J. Jang, K. Cho, T.-Y. Kim, J.-K. Kim, Y. Song, W.-K. Hong, M. Min, H. Lee, T. Lee, *Nanoscale* **2015**, 7, 18780.

- [51] X. Liu, J. Gu, K. Ding, D. Fan, X. Hu, Y.-W. Tseng, Y.-H. Lee, V. Menon, S. R. Forrest, *Nano Lett.* **2017**, 17, 3176.
- [52] S. Véléz, D. Ciudad, J. Island, M. Buscema, O. Txoperena, S. Parui, G. A. Steele, F. Casanova, H. S. J. Van Der Zant, A. Castellanos-Gomez, L. E. Hueso, *Nanoscale* **2015**, 7, 15442.
- [53] D. B. Sulas-Kern, E. M. Miller, J. L. Blackburn, *Energy Environ. Sci.* **2020**, 13, 2684.
- [54] S. Blumstengel, S. Sadofev, C. Xu, J. Puls, F. Henneberger, *Phys. Rev. Lett.* **2006**, 97, 237401.
- [55] S. Blumstengel, S. Sadofev, F. Henneberger, *New J. Phys.* **2008**, 10, 065010.
- [56] G. Itskos, X. Xristodoulou, E. Iliopoulos, S. Ladas, S. Kennou, M. Neophytou, S. Choulis, *Appl. Phys. Lett.* **2013**, 102, 063303.
- [57] F. Bianchi, S. Sadofev, R. Schlesinger, B. Kobin, S. Hecht, N. Koch, F. Henneberger, S. Blumstengel, *Appl. Phys. Lett.* **2014**, 105, 233301.
- [58] R. Schlesinger, F. Bianchi, S. Blumstengel, C. Christodoulou, R. Ovsyannikov, B. Kobin, K. Moudgil, S. Barlow, S. Hecht, S. R. Marder, F. Henneberger, N. Koch, *Nat. Commun.* **2015**, 6, 6754.
- [59] M. Eyer, J. Frisch, S. Sadofev, N. Koch, E. J. W. List-Kratochvil, S. Blumstengel, *J. Phys. Chem. C* **2017**, 121, 21955.
- [60] S. Blumstengel, N. Koch, *Optoelectronic Organic-Inorganic Semiconductor Heterojunctions*, CRC Press, Boca Raton **2021**.
- [61] 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.
- [62] J. Ma, P. Amsalem, T. Schultz, D. Shin, X. Xu, N. Koch, *Adv. Electron. Mater.* **2021**, 7, 2100425.
- [63] C. Ludwig, B. Gompf, J. Petersen, R. Strohmaier, W. Eisenmenger, *Z. Phys. B: Condens. Matter* **1994**, 93, 365.
- [64] Y. Azuma, T. Hasebe, T. Miyamae, K. K. Okudaira, Y. Harada, K. Seki, E. Morikawa, V. Saile, N. Ueno, *J. Synchrotron Radiat.* **1998**, 5, 1044.
- [65] Y. Azuma, S. Akatsuka, K. K. Okudaira, Y. Harada, N. Ueno, *J. Appl. Phys.* **2000**, 87, 766.
- [66] H. Yamane, S. Kera, K. K. Okudaira, D. Yoshimura, K. Seki, N. Ueno, *Phys. Rev. B* **2003**, 68, 033102.
- [67] K. Kamiya Okudaira, S. Hasegawa, H. Ishii, K. Seki, Y. Harada, N. Ueno, *J. Appl. Phys.* **1999**, 85, 6453.
- [68] M. Momose, K. Kamiya, K. Sugita, N. Ueno, *Jpn. J. Appl. Phys.* **1994**, 33, 4754.
- [69] J. Choi, H. Zhang, J. H. Choi, *ACS Nano* **2016**, 10, 1671.
- [70] J. Pak, M. Min, K. Cho, D.-H. Lien, G. H. Ahn, J. Jang, D. Yoo, S. Chung, A. Javey, T. Lee, *Appl. Phys. Lett.* **2016**, 109, 183502.
- [71] P. Choudhury, L. Ravavarapu, R. Dekle, S. Chowdhury, *J. Phys. Chem. C* **2017**, 121, 2959.
- [72] G. Ghimire, S. Adhikari, S. G. Jo, H. Kim, J. Jiang, J. Joo, J. Kim, *J. Phys. Chem. C* **2018**, 122, 6794.
- [73] Y. Huang, F. Zhuge, J. Hou, L. Lv, P. Luo, N. Zhou, L. Gan, T. Zhai, *ACS Nano* **2018**, 12, 4062.
- [74] K. Greulich, A. Belser, S. Bölke, P. Grüninger, R. Karstens, M. S. Sättele, R. Ovsyannikov, E. Giangrisostomi, T. V. Basova, D. Klyamer, T. Chassé, H. Peisert, *J. Phys. Chem. C* **2020**, 124, 16990.
- [75] S. H. Amsterdam, T. K. Stanev, L. Wang, Q. Zhou, S. Irgen-Gioro, S. Padgaonkar, A. A. Murthy, V. K. Sangwan, V. P. Dravid, E. A. Weiss, P. Darancet, M. K. Y. Chan, M. C. Hersam, N. P. Stern, T. J. Marks, *J. Am. Chem. Soc.* **2021**, 143, 17153.
- [76] C. Ruppert, A. Chernikov, H. M. Hill, A. F. Rigosi, T. F. Heinz, *Nano Lett.* **2017**, 17, 644.
- [77] M. R. Habib, H. Li, Y. Kong, T. Liang, S. M. Obaidulla, S. Xie, S. Wang, X. Ma, H. Su, M. Xu, *Nanoscale* **2018**, 10, 16107.
- [78] S. Wang, C. Chen, Z. Yu, Y. He, X. Chen, Q. Wan, Y. Shi, D. W. Zhang, H. Zhou, X. Wang, P. Zhou, *Adv. Mater.* **2019**, 31, 1806227.
- [79] M. R. Habib, W. Wang, A. Khan, Y. Khan, S. M. Obaidulla, X. Pi, M. Xu, *Adv. Theor. Simul.* **2020**, 3, 2000045.
- [80] S. M. Obaidulla, M. R. Habib, Y. Khan, Y. Kong, T. Liang, M. Xu, *Adv. Mater. Interfaces* **2020**, 7, 1901197.
- [81] K. Rijal, F. Rudayni, T. R. Kafle, W.-L. Chan, *J. Phys. Chem. Lett.* **2020**, 11, 7495.
- [82] O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, A. Kis, *Nat. Nanotechnol.* **2013**, 8, 497.
- [83] H. S. Nalwa, *RSC Adv.* **2020**, 10, 30529.
- [84] A. Taffelli, S. Dirè, A. Quaranta, L. Pancheri, *Sensors* **2021**, 21, 2758.
- [85] J. F. Gonzalez Marin, D. Unuchek, K. Watanabe, T. Taniguchi, A. Kis, *npj 2D Mater. Appl.* **2019**, 3, 14.
- [86] Chandan, S. Sarkar, B. Angadi, *Appl. Phys. Lett.* **2021**, 118, 172105.
- [87] A. George, M. V. Fistul, M. Gruenewald, D. Kaiser, T. Lehnert, R. Mupparapu, C. Neumann, U. Hübner, M. Schaal, N. Masurkar, L. M. R. Arava, I. Staude, U. Kaiser, T. Fritz, A. Turchanin, *npj 2D Mater. Appl.* **2021**, 5, 15.
- [88] Y.-C. Wu, C.-H. Liu, S.-Y. Chen, F.-Y. Shih, P.-H. Ho, C.-W. Chen, C.-T. Liang, W.-H. Wang, *Sci. Rep.* **2015**, 5, 11472.
- [89] D. Kufer, G. Konstantatos, *Nano Lett.* **2015**, 15, 7307.
- [90] S. Dalgleish, L. Reissig, Y. Shuku, G. Ligorio, K. Awaga, E. J. W. List-Kratochvil, *Sci. Rep.* **2019**, 9, 16682.
- [91] M. Raoufi, S. Rühl, S. Chandrabose, A. Shukla, B. Sun, E. List-Kratochvil, S. Blumstengel, D. Neher, *Phys. Status Solidi A* **2023**, 2300107.
- [92] S. Heutz, S. M. Bayliss, R. L. Middleton, G. Rumbles, T. S. Jones, *J. Phys. Chem. B* **2000**, 104, 7124.
- [93] S. Yim, S. Heutz, T. S. Jones, *J. Appl. Phys.* **2002**, 91, 3632.
- [94] M. Ichikawa, *Thin Solid Films* **2013**, 527, 239.
- [95] R. Canton-Vitoria, H. B. Gobeze, V. M. Blas-Ferrando, J. Ortiz, Y. Jang, F. Fernández-Lázaro, Á. Sastre-Santos, Y. Nakanishi, H. Shinohara, F. D'souza, N. Tagmatarchis, *Angew. Chem., Int. Ed.* **2019**, 58, 5712.
- [96] F. Piersimoni, R. Schlesinger, J. Benduhn, D. Spoltore, S. Reiter, I. Lange, N. Koch, K. Vandewal, D. Neher, *J. Phys. Chem. Lett.* **2015**, 6, 500.
- [97] T. Zhu, L. Yuan, Y. Zhao, M. Zhou, Y. Wan, J. Mei, L. Huang, *Sci. Adv.* **2018**, 4, eaao3104.
- [98] C.-H. Cheng, D. Cordovilla Leon, Z. Li, E. Litvak, P. B. Deotare, *ACS Nano* **2020**, 14, 10462.
- [99] M. Raoufi, S. Chandrabose, R. Wang, B. Sun, N. Z. Morales, S. Shoaee, S. Blumstengel, N. Koch, E. List-Kratochvil, D. Neher, *J. Phys. Chem. C* **2023**, 127, 5866.
- [100] R. A. Marcus, *J. Chem. Phys.* **1965**, 43, 679.
- [101] J. Wang, T. Ding, K. Gao, L. Wang, P. Zhou, K. Wu, *Nat. Commun.* **2021**, 12, 6333.
- [102] M. Möbus, N. Karl, T. Kobayashi, *J. Cryst. Growth* **1992**, 116, 495.
- [103] W. Zhao, Z. Ghorannevis, L. Chu, M. Toh, C. Kloc, P.-H. Tan, G. Eda, *ACS Nano* **2013**, 7, 791.
- [104] N. Koch, *ChemPhysChem* **2007**, 8, 1438.
- [105] A. Kahn, N. Koch, W. Gao, *J. Polym. Sci., Part B: Polym. Phys.* **2003**, 41, 2529.
- [106] Y. Nakayama, S. Kera, N. Ueno, *J. Mater. Chem. C* **2020**, 8, 9090.
- [107] R. Nitsche, T. Fritz, *Phys. Rev. B*, **2004**, 70, 195432.
- [108] M. Schneider, E. Umbach, M. Sokolowski, *Chem. Phys.* **2006**, 325, 185.
- [109] H. Proehl, T. Dienel, R. Nitsche, T. Fritz, *Phys. Rev. Lett.* **2004**, 93, 097403.
- [110] M. Hoffmann, K. Schmidt, T. Fritz, T. Hasche, V. M. Agranovich, K. Leo, *Chem. Phys.* **2000**, 258, 73.
- [111] T. Korn, S. Heydrich, M. Hirmer, J. Schmutzler, C. Schüller, *Appl. Phys. Lett.* **2011**, 99, 102109.
- [112] E. Engel, K. Leo, M. Hoffmann, *Chem. Phys.* **2006**, 325, 170.
- [113] S. H. Aleithan, M. Y. Livshits, S. Khadka, J. J. Rack, M. E. Kordes, E. Stinaff, *Phys. Rev. B* **2016**, 94, 035445.

- [114] H. Shi, R. Yan, S. Bertolazzi, J. Brivio, B. Gao, A. Kis, D. Jena, H. G. Xing, L. Huang, *ACS Nano* **2013**, 7, 1072.
- [115] H. Wang, C. Zhang, F. Rana, *Nano Lett.* **2015**, 15, 339.
- [116] E. A. A. Pogna, M. Marsili, D. De Fazio, S. Dal Conte, C. Manzoni, D. Sangalli, D. Yoon, A. Lombardo, A. C. Ferrari, A. Marini, G. Cerullo, D. Prezzi, *ACS Nano* **2016**, 10, 1182.
- [117] R. R. Lunt, J. B. Benziger, S. R. Forrest, *Adv. Mater.* **2010**, 22, 1233.
- [118] H. Kuhn, *J. Chem. Phys.* **1970**, 53, 101.
- [119] K. M. Goodfellow, C. Chakraborty, K. Sowers, P. Waduge, M. Wanunu, T. Krauss, K. Driscoll, A. N. Vamivakas, *Appl. Phys. Lett.* **2016**, 108, 021101.
- [120] F. Prins, A. J. Goodman, W. A. Tisdale, *Nano Lett.* **2014**, 14, 6087.
- [121] A. Raja, A. Montoya–Castillo, J. Zultak, X.-X. Zhang, Z. Ye, C. Roquet, D. A. Chenet, A. M. Van Der Zande, P. Huang, S. Jockusch, J. Hone, D. R. Reichman, L. E. Brus, T. F. Heinz, *Nano Lett.* **2016**, 16, 2328.
- [122] T. Förster, *Ann. Phys.* **1948**, 437, 55.
- [123] J. J. Rindermann, G. Pozina, B. Monemar, L. Hultman, H. Amano, P. G. Lagoudakis, *Phys. Rev. Lett.* **2011**, 107, 236805.
- [124] D. Basko, G. C. La Rocca, F. Bassani, V. M. Agranovich, *Eur. Phys. J. B* **1999**, 8, 353.
- [125] A. J. Lovinger, S. R. Forrest, M. L. Kaplan, P. H. Schmidt, T. Venkatesan, *J. Appl. Phys.* **1984**, 55, 476.



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