

Effect of the Interfacial Energy Landscape on Photo-induced Charge Generation at the ZnPc-MoS₂ Interface

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Abstract

Monolayer transition-metal dichalcogenide crystals (TMDC) can be combined with other functional materials, such as organic molecules, to form a wide range of heterostructures with tailorable properties. Although a number of works have shown that ultrafast charge transfer (CT) can occur at organic-TMDC interfaces, conditions that would facilitate the separation of interfacial CT excitons into free carriers remain unclear. Here, time-resolved and steady-state photoemission spectroscopy are used to study the potential energy landscape, charge transfer and exciton dynamics at the zinc phthalocyanine (ZnPc)/monolayer (ML) MoS₂ and ZnPc/bulk MoS₂ interfaces. Surprisingly, although both interfaces have a type-II band alignment and exhibit sub-100 femtosecond CT, the CT excitons formed at the two interfaces show drastically different evolution dynamics. The ZnPc/ML-MoS₂ behaves like typical donor-acceptor interfaces in which CT excitons dissociate into electron-hole pairs. On the contrary, back electron transfer occurs at ZnPc/bulk-MoS₂, which results in the formation of triplet excitons in ZnPc. The difference can be explained by the different amount of band bending found in the ZnPc film deposited on ML-MoS₂ and bulk-MoS₂. Our work illustrates that the potential energy landscape near the interface plays an important role in the charge separation behavior. Therefore, considering the energy level alignment at the interface alone is not enough for predicting whether free charges can be generated effectively from an interface.

INTRODUCTION

Layered two-dimensional (2D) materials such as transition metal dichalcogenide crystals (TMDCs) have attracted much attention recently because they allow materials properties to be tailored by stacking different atomically thin crystals together.¹⁻³ This “stackability” is enabled by the weak van der Waals (vdW) bonding between layers and the absence of dangling bonds at the interface. Similar to TMDCs, organic molecules are bonded together by vdW forces. Hence, organic molecules can be combined readily with TMDCs to produce heterostructures that possess advantages of both materials.⁴⁻⁷ For instance, organic molecules are excellent light absorbers and the thickness of an organic film can be controlled easily. They can be combined with TMDCs, which have outstanding and gate-tunable carrier mobility, to produce sensitive detectors and gate-tunable p-n junctions.⁸⁻¹⁴ More excitingly, the hybrid system can realize new properties and functionalities that neither materials can provide. For example, atomically-thin lateral¹⁵ and vertical p-n junctions¹⁶ can be fabricated in a scalable fashion by doping TMDCs with organic molecules. Combining organic molecules with other layered materials such as Bi₂Se₃ can create exotic systems such as lateral topological p-n junctions.^{17,18} Moreover, organic molecules can passivate defects in TMDCs *via* either physical¹⁹ or chemical adsorption,^{20,21} which is important for improving the carrier mobility in TMDCs. Technically, large area organic-TMDC heterostructures can be synthesized readily in a scalable fashion.

Recent works have shown that femtosecond (fs) to picosecond (ps) charge transfer (CT) can occur across some organic-TMDC interfaces.²²⁻²⁷ However, CT across the interface is only the first step for generating free carriers from bound excitons. The CT process will likely produce Coulombic-bound electron-hole pairs at the interface (commonly known as CT excitons or indirect excitons).²⁸ The relaxation and dissociation mechanisms of these CT excitons at the interface are

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3 not well-understood. In most applications, it is desired that these CT excitons can dissociate
4 effectively into free electron-hole pairs. However, other competing electronic processes would
5 occur prior to the exciton dissociation. In fact, the separation of CT excitons into free carriers is
6 known to be a process that would limit the performance of organic photovoltaics^{29,30} and possibly
7 optoelectronic devices made with other excitonic materials. Therefore, identifying conditions that
8 would favor effective exciton dissociation is of paramount importance for fabricating effective
9 devices based on organic-TMDC heterostructures.

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19 Although a type-II band alignment generally enables effective CT across the interface, the
20 subsequent evolution of the CT exciton, which plays an important role in the generation of free
21 charges, is a more complicated process that depends critically on the potential energy landscape
22 near the interface. Unfortunately, very few works directly measure both the energy landscape near
23 the interface and the evolution dynamics of the CT exciton. Without knowing the correlation
24 between the two at the molecular level, designing interfaces for effective exciton dissociation
25 remains a trial-and-error task. Here, by using zinc phthalocyanine (ZnPc)/MoS₂ interface as a
26 prototype system, we illustrate the importance of the band bending, in addition to the interfacial
27 energy level alignment, on the spatial range of coherent CT and the evolution of the CT exciton.
28 In particular, we compare the exciton dynamics at ZnPc/monolayer (ML)-MoS₂ and ZnPc/bulk-
29 MoS₂ interfaces. Surprisingly, the two seemingly similar interfaces show distinctly different
30 charge separation behaviors. Although both interfaces has a type-II band alignment, our
31 photoemission spectroscopy measurement shows that the two possess different amount of band
32 bending in the ZnPc film near the interface. Because of the differences in the band bending and
33 the spin lifetime in ML-MoS₂ and bulk-MoS₂,^{31,32} CT excitons at the ZnPc/bulk-MoS₂ interface
34 recombine to form triplet (T₁) exciton *via* back electron transfer, while CT excitons at the
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ZnPc/ML-MoS₂ interface can separate into free carriers. Despite both interfaces exhibit sub-100 fs CT, the very different evolution dynamics of the CT exciton implies that the two interfaces can be suitable for different applications. For instance, the ZnPc/bulk-MoS₂ interface can be used for triplet sensitization,³³ while the ZnPc/ML-MoS₂ interface can be used for effective charge separation.

EXPERIMENTAL METHODS

Sample Preparation. Commercially available, high quality, CVD-grown ML-MoS₂ on SiO₂/Si (6Carbon Technology, Shenzhen) was used. The ML-MoS₂ layer has a continuous coverage and a microscopy image of these samples is shown in the supporting information (Fig. S1). For bulk-MoS₂, a cm-sized single crystal purchased from SPI supplies was used. Before the measurement, the MoS₂ samples were annealed at 400°C for 12 hours in an ultrahigh vacuum chamber (UHV) with a base pressure of 1×10^{-10} Torr. The quality of our bulk-MoS₂ sample was reported previously in Ref. [24]. For the ML-MoS₂ sample, angle-resolved photoemission spectroscopy (ARPES) was used to characterize the band structure of the material. A clear band-structure was observed in the ARPES experiment (supporting information, Fig. S2), indicating that the ML-MoS₂ has a continuous coverage, good crystallinity and a clean surface. The valence band (VB) edge at the K point is located at a slightly higher energy than the VB edge at the Γ point, which is a characteristic feature of ML-MoS₂.^{34,35} The ML-MoS₂ has a photoluminescence (PL) peak at ~ 660 nm (supporting information, Fig. S3), which is consistent to the properties of ML-MoS₂.³⁶ Furthermore, the CVD-grown ML-MoS₂ has an exciton decay dynamics that is comparable to that of a mechanically exfoliated ML-MoS₂ sample obtained from a bulk-MoS₂ crystal (supporting information, Fig. S4).

After the bare MoS₂ surface was annealed, it was then transferred *in-situ* to another UHV chamber with a base pressure of 1×10^{-9} Torr for ZnPc deposition. The nominal thickness of the ZnPc film was monitored by a quartz crystal microbalance. The uncertainty in the nominal thickness measured by this method was $\sim 5 - 10$ %, which was mainly originated from the uncertainty in determining the mass density of the film. A film density of 1.55 g cm^{-3} was used to calculate the film thickness. For thicknesses up to 4 nm, a substrate temperature of 90 °C and a deposition rate of 0.3 Å/min were used. These conditions are known to produce a uniform ZnPc

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3 film with molecules having a face-on orientation.³⁷ The ZnPc orientation can be verified using
4 ultraviolet photoemission spectroscopy (UPS)^{38,39} and we found that ZnPc molecules in our films
5 have a face-on orientation (supporting information, Fig. S5). For film thicknesses larger than 4
6 nm, a faster deposition rate of 0.8 Å/min was used and the sample was kept at room temperature.
7 After ZnPc deposition, the sample was transferred back to the photoemission chamber where the
8 photoemission experiments were performed.

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11 **ARPES and UPS Spectroscopy.** In the UPS and ARPES measurements, UV light
12 generated from a standard UV lamp was used to ionize electrons from the sample. The He-I
13 emission line with a photon energy of 21.22 eV was used. The energy and the emission angle of
14 photoelectrons were measured using a hemispherical analyzer equipped with an imaging detector
15 (Phoibos 100, SPECS).

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18 **Time-resolved Two Photon Photoemission (TR-TPPE) Spectroscopy.** TR-TPPE
19 spectroscopy was used to measure the excited state dynamics of the sample. The details of the TR-
20 TPPE setup can be found in our previous publication.⁴⁰ In short, the TR-TPPE is a pump-probe
21 spectroscopy technique in which the energy and population of excited electrons were measured by
22 using photoemission spectroscopy. In this work, the pump and probe beam have a photon energy
23 of 1.77 eV and 4.68 eV respectively. The pump and probe beams were generated by using the
24 outputs of two non-collinear optical parametric amplifiers (NOPA), which were pumped by a
25 Yb:KGW regenerative amplifier running at 125 kHz (Pharos, 10 W, Light Conversion). The pump
26 and probe beams have a pulse duration of 25 fs and 65 fs respectively. The beams have a Gaussian
27 profile with a full width half maxima (fwhm) size of ~ 0.8 mm. The kinetic energy of the
28 photoelectrons ionized by the probe beam was measured by the aforementioned hemispherical
29 electron analyzer. The measurement was done at room temperature.

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32 **Transient Absorption Measurement.** In the transient absorption measurements, an 80-
33 MHz Ti:sapphire oscillator produces ~100 fs pulses at about 840 nm. Part of this beam was focused
34 to a BBO crystal to generate its second harmonic at 420 nm, which is used as the probe pulse. The
35 rest of the 840-nm beam was coupled to a photonic crystal fiber to generate a broadband
36 supercontinuum. A bandpass filter with a bandwidth of 10 nm was used to select the 710 nm
37 component of the supercontinuum, which serves as the pump pulse. The two pulses are combined
38 by a beam splitter and co-focused by a microscope objective lens to the sample surface with a spot
39 size of about 2 μm. We measured differential reflection of the probe as a function of the probe
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3 delay. The differential reflection is defined as $\Delta R/R_0 = (R - R_0)/R_0$, where R and R_0 are the reflection
4 coefficient of the sample at the probe wavelength. To measure this quantity, the probe beam
5 reflected by the sample was sent to a silicon photodiode, which output was detected by a lock-in
6 amplifier. A mechanical chopper was used in the pump arm to modulate the pump intensity at
7 about 2 kHz, for the lock-in detection. The time delay between the pump and probe pulses was
8 controlled by changing the path length of the pump beam by using a linear stage. All measurements
9 were performed with the sample at room temperature.
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16 17 **RESULTS AND DISCUSSION**

18 19 **Interfacial band alignment and band bending**

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21 Because the interfacial band alignment and the band bending play important roles in the
22 CT and exciton dissociation dynamics, we will first discuss the band structure of the ZnPc/ML-
23 MoS₂ and the ZnPc/bulk-MoS₂ interfaces measured by the UPS experiment. One of the major
24 differences in the band structure between ML-MoS₂ and bulk-MoS₂ is that the energy of the
25 valence band (VB) edge at the Γ point increases with the number of MoS₂ layers because of the
26 interlayer electronic coupling.^{34,41} The energy upshift, from ML to bulk, of the VB-edge at the Γ
27 point results in the well-known transition from a direct to an indirect gap semiconductor.³⁶ Figure
28 1a compares the UPS spectra of our ML-MoS₂ and bulk-MoS₂ samples measured at the Γ point.
29 The energy is referenced with respect to the Fermi level (E_f). The VB-edge at the Γ point of the
30 bulk-MoS₂ is ≈ 0.65 eV higher than that of the ML-MoS₂, which agrees well with first principle
31 calculation³⁴ and micro-ARPES measurement.³⁵ The positions of the VB-edges with respect to the
32 E_f for ML- and bulk-MoS₂ are shown in Fig. 1b. We further note that both samples have similar
33 workfunctions (ML: 4.55 eV; bulk: 4.65 eV). Hence, a similar energy upshift in the VB-edges can
34 be obtained if the energy is referenced with respect to the vacuum level. For bulk-MoS₂, the VB-
35 edge at the Γ point is the valence band maxima (VBM). For the ML-MoS₂ sample, we found that
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the band edge at the Γ point is slightly lower than that at the K point, which is consistent with previous theoretical and experimental works.^{34,35,41} The angle-resolved spectra are shown in the Fig. S2 in the supporting information. Figure 1b summarizes the key differences between the band structure of our ML and bulk MoS₂ samples. Positions of the conduction band minimum (CBM) are assigned based on reported transport gaps of ML and bulk MoS₂.^{34,42}

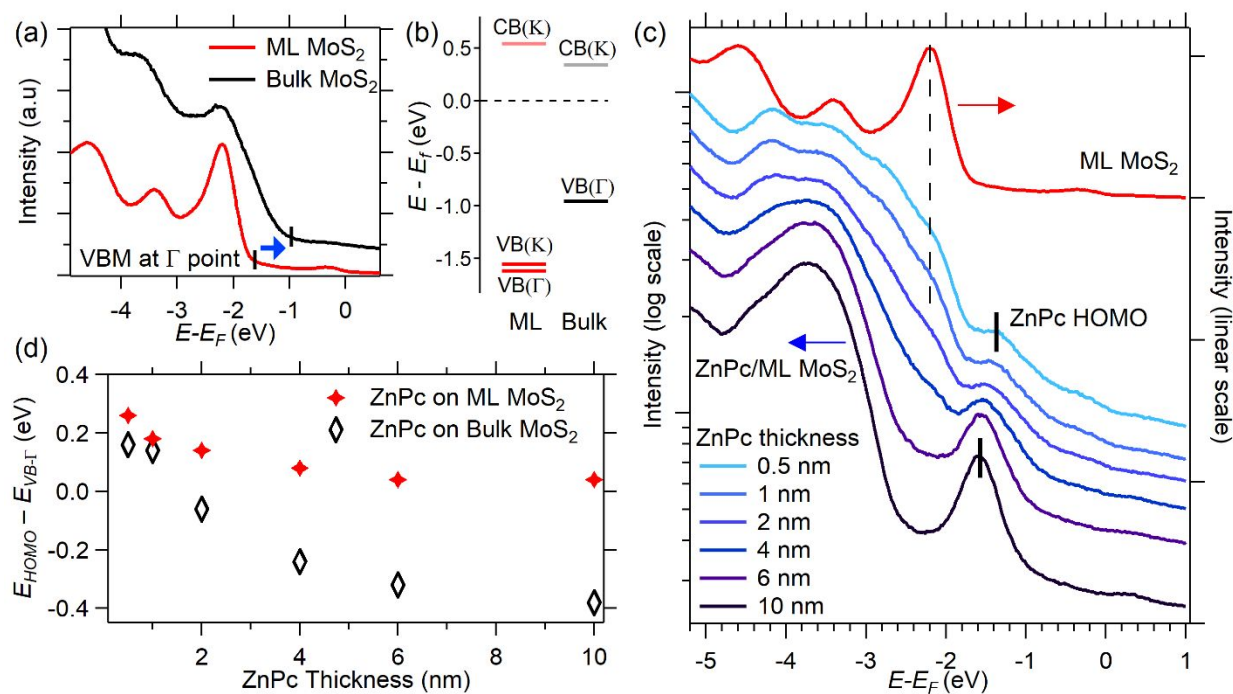


Figure 1: (a) The UPS spectra for ML and bulk MoS₂ at the Γ point. The VB-edges are indicated by the vertical bars. (b) A comparison between the band structure of ML and bulk MoS₂. (c) The UPS spectra for ZnPc/ML-MoS₂ with various ZnPc's thickness. The position of the ZnPc's HOMO peak is indicated by the vertical bars. For comparison, the spectrum for the ML-MoS₂ is also shown (red line). The spectra for the ZnPc/ML-MoS₂ samples are plotted in a log scale such that features from both layers can show up clearly in the 0.5 nm and 1 nm spectra. (d) The HOMO-VB edge offset at ZnPc/ML-MoS₂ and ZnPc/bulk-MoS₂ interfaces as a function of the ZnPc's thickness.

If all the energy levels are aligned using a common vacuum level, one would anticipate that the energy offsets between the MoS₂'s VB-edge and the ZnPc's HOMO would be very different for the ZnPc/ML-MoS₂ and the ZnPc/bulk MoS₂ interfaces. This is because the energy of the VBM of ML and bulk MoS₂ differs by ≈ 0.6 eV (Fig. 1b). However, surprisingly, a very

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3 similar energy offset (in the range of 0.2 - 0.3 eV) is observed for both interfaces (ZnPc/ML-MoS₂,
4 ZnPc/bulk-MoS₂). Figure 1c shows the UPS spectra of the ML-MoS₂ sample with various ZnPc
5 thicknesses as ZnPc molecules are deposited consecutively on the MoS₂ surface. The ZnPc's
6 HOMO peaks (vertical bars) can be identified for a nominal thickness as small as 0.5 nm. For
7 comparison, the spectrum for the bare ML-MoS₂ is also shown (red line). The first major peak in
8 the MoS₂ valence band (dashed line) is still visible in the ZnPc/MoS₂ spectra for small ZnPc
9 thicknesses. The offset between the ZnPc's HOMO and the MoS₂'s VB-edge at the Γ -point is 0.26
10 eV. With an increase in the ZnPc thickness, the HOMO peak shifts to a slightly lower energy (i.e.
11 a larger binding energy). The energy offset ($E_{HOMO} - E_{VB-\Gamma}$) as a function of ZnPc thickness is
12 plotted in Fig. 1d. For comparison, we have also included the energy offset for the ZnPc/bulk-
13 MoS₂ interface that are reported in our pervious study.²⁴

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29 Two important observations stem from the above comparison. First, for small ZnPc
30 thicknesses (0.5 – 1 nm), both interfaces show a very similar energy offset. As mentioned earlier,
31 this is rather surprising because the energy of the VB-edge at the Γ point for ML MoS₂ is
32 significantly lower than that for bulk MoS₂ (Fig. 1b). The physical origin of this observed
33 “pinning” in the VB-HOMO offset is not clear, but we speculate that it would be resulted from the
34 orbital mixing between MoS₂ and ZnPc considering that the MoS₂ orbit at the Γ -point has a strong
35 out-of-plane character.³⁴ Based on this offset, both ZnPc/ML-MoS₂, ZnPc/bulk-MoS₂ interfaces
36 have a type-II band alignment. The type-II band alignment is consistent with other reports on the
37 metal-Pc/ML-MoS₂ interface.^{27,43-45} Second, there is a much stronger band bending in the ZnPc
38 film deposited on bulk-MoS₂ than on ML-MoS₂. It is known that ZnPc molecules on MoS₂ have
39 a face-on orientation.⁴⁶ For this orientation, our previous studies⁴⁷ found that the position of the
40 HOMO peak is in the range of 1.2 - 1.5 eV below the E_f and the workfunction is in the range of
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3 4.3 - 4.5 eV. Comparing these numbers with the VB-edge position of the bulk-MoS₂ (Fig. 1b), one
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5 can find that if the energy offset between ZnPc's HOMO and MoS₂'s VB-edge is pinned at ~0.2 -
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7 0.3 eV, the E_f of ZnPc would be much higher than that of bulk-MoS₂. Thus, ground state electron
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9 transfer from ZnPc to bulk-MoS₂ needs to occur in order to produce the observed energy level
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11 alignment. The expected ground state electron transfer is indeed consistent with the strong band
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13 bending observed in ZnPc deposited on bulk-MoS₂. The direction of the band bending indicates
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15 that net positive charges are accumulated in the ZnPc layer.⁴⁸ The different amount of the band
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17 bending for ZnPc/ML-MoS₂ and ZnPc/bulk-MoS₂ interfaces should have a strong influence on the
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19 CT and the subsequent evolution of the CT states.
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23 **Charge Transfer Excitons at the ZnPc/ML-MoS₂ interface**

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26 The ZnPc/ML-MoS₂ interface has a type-II band alignment, which should allow ultrafast
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28 electron transfer from ZnPc to ML-MoS₂. Figure 2a shows the TR-TPPE spectrum of a 1 nm
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30 ZnPc/ML-MoS₂ sample. In the TR-TPPE experiment, the sample is excited by a 1.77 eV pump
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32 beam. This photon energy is enough to excite the S₁ state of ZnPc,⁴⁹ but it is below the optical
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34 band gap of the ML-MoS₂.³⁶ One of the unique advantages of the TR-TPPE spectroscopy is that
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36 it measures the energy of excited states directly. On the vertical axis in Fig. 2a, the energy of
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38 excited states is referenced with respect to the ZnPc's HOMO position determined from our UPS
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40 experiment. The pseudocolor represents the pump-induced photoemission intensity. At delay time
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42 $t \approx 0$ ps, a peak at ≈ 1.75 eV is observed. Figure 2b shows the spectra at various delay times and
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44 the peak at $E - E_{HOMO} \approx 1.75$ eV is apparent in the 0.01 ps and 0.03 ps spectra. We attribute this
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46 peak to the S₁ state of ZnPc because the peak position agrees well with the energy of the S₁ exciton.
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48 Note that it cannot be originated from excitons in ML-MoS₂ because in a control experiment
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50 conducted on the bare MoS₂ sample, we observe negligible TR-TPPE signal (supporting
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information, Fig. S6). This is reasonable because the pump photon energy is less than the bandgap of ML-MoS₂. This S₁ state decays rapidly on a sub-100 fs timescale (Fig. 2c, open squares). The decay of the S₁ population can be attributed to the electron transfer from ZnPc to MoS₂.^{24,50} In our TR-TPPE setup, the pump-probe cross-correlation has a fwhm width of 70 fs (Fig. 2c, solid black line). Fitting the S₁ decay to a single exponential decay convoluted with the widths of the pump and probe pulses yields a CT time of 40 fs (dashed line).

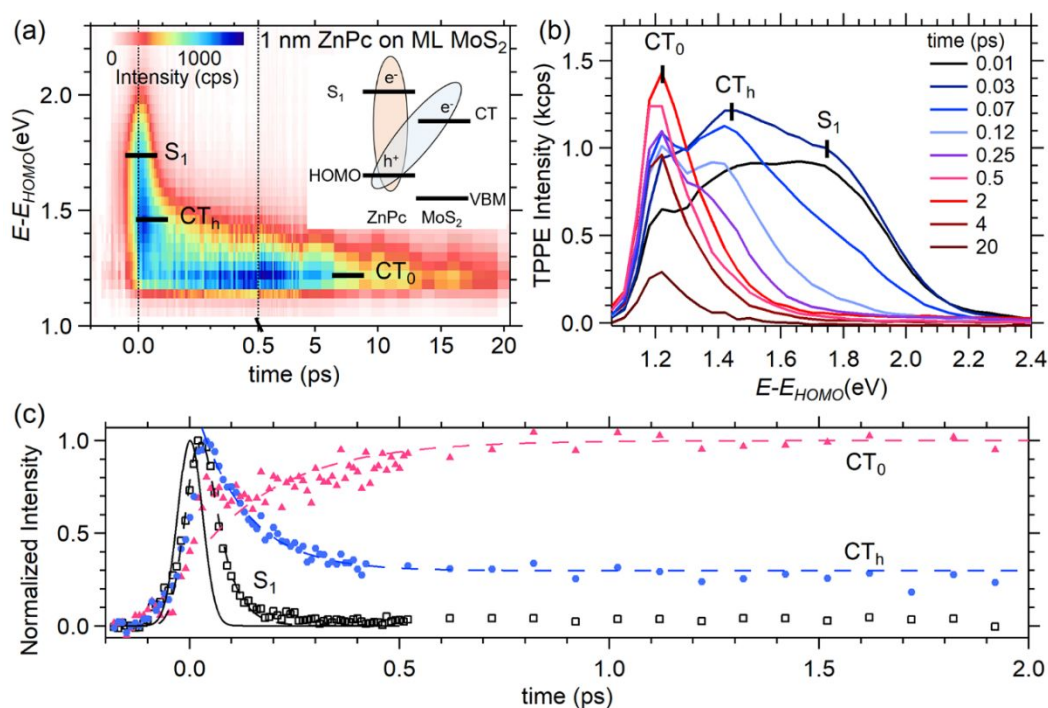


Figure 2: (a) TR-TPPE spectrum of the 1 nm-ZnPc/ML-MoS₂ sample. The pump beam excites the ZnPc film selectively and the interfacial CT exciton is produced by electron transfer from ZnPc to MoS₂. The time axis is split at 0.5 ps in order to show the dynamics on two different timescales. The inset is a schematic diagram showing the energy level alignment at the interface, ZnPc's S₁ exciton and CT excitons. (b) TPPE spectra at some selected pump-probe delay times. The positions for the S₁, CT_h and CT₀ states are shown. (c) The intensity of the S₁, CT_h and CT₀ states as a function of time. The solid black line shows the pump-probe cross-correlation. The lifetime of the S₁ state is fit by a rate equation model that accounts for the pulse width of pump and probe pulses (black dashed line). The blue and red dashed line are fits to single exponential decay and single exponential rise respectively.

Another peak located at ≈ 0.2 eV below the S₁ peak can be found in the spectrum. This state has a slightly delayed intensity rise (Fig. 2c, solid circle) and a longer lifetime as compared

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3 to the S_1 peak. A fit to an exponential decay yields a lifetime of 120 fs (Fig 2c, blue dashed line).
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5 We assign this state to a hot charge transfer state (CT_h) that consists of a pair of Coulombic-bound
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7 electron and hole in MoS_2 and ZnPc respectively (inset in Fig. 2a). Similar CT exciton states
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9 unveiled by optical absorption spectroscopy has been reported recently for the CuPc/ MoS_2
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11 interface.⁴⁵ The CT state can be populated by the CT from ZnPc to MoS_2 . The energy of this state
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13 is ≈ 1.7 eV above the MoS_2 's VBM (1.44 eV with respect to the ZnPc's HOMO). This energy is
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15 slightly lower compared to the A-exciton energy of ML- MoS_2 (1.87 eV), but it is within our
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17 experimental uncertainty ($\sim \pm 0.1$ eV). In our experiment, error would be introduced in determining
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19 the relative energy position of the HOMO (in the UPS spectrum) and the excited state (in the TPPE
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21 spectrum) because different light sources used in the two experiments would introduce different
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23 sample charging conditions. The slightly lower energy of the CT exciton indicates that it would
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25 have a larger binding energy as compared to the A-exciton of MoS_2 , which can be resulted from
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27 the more localized nature of the molecular orbit. Finally, a state at $E - E_{HOMO} \approx 1.22$ eV can be
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29 found, which clearly shows a delayed population rise. The rise time of this state is 200 fs (Fig. 2c,
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31 red dashed line). This state can be populated from the relaxation of the CT_h state. Following
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33 previous TR-TPPE works on other donor-acceptor interfaces,⁵¹⁻⁵³ we assign this peak to a relaxed,
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35 localized CT state (CT_0).
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42 Moreover, we note that the probe photons (4.68 eV) used in our experiment do not have a
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44 large enough in-plane momentum to ionize excited electrons residing at the K-valleys of MoS_2 *via*
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46 a direct optical process.^{54,55} However, as mentioned earlier, it is likely that the electron in these CT
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48 excitons localizes spatially and do not have a well-defined momentum vector in the k -space.
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50 Hence, the momentum conservation requirement for photoionization cannot be applied to this case.
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52 We will come back to this point when the lifetime of the CT_0 state is discussed.
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Comparison of the coherent CT range between ZnPc/ML-MoS₂ and ZnPc/bulk-MoS₂

Previously, we have reported that sub-100 fs electron transfer from ZnPc to MoS₂ can also occur at the ZnPc/bulk-MoS₂ interface.²⁴ Hence, ultrafast CT can occur at both ZnPc/ML-MoS₂ and ZnPc/bulk-MoS₂ interfaces, which is consistent with the similar ZnPc-HOMO/MoS₂-VBM offset found for both interfaces. However, when the ZnPc film becomes thicker, we find that there is a subtle difference in the spatial range of the CT, i.e. the distance from the interface in which the ultrafast CT would still occur. Figure 3a and 3b show the temporal evolution of the normalized S₁ peak intensity for ZnPc/ML-MoS₂ and ZnPc/bulk MoS₂ samples with various ZnPc film thicknesses. Because photoemission is a surface sensitive technique, it mainly probes the population of excitons near the ZnPc surface. By varying the thickness of the ZnPc layer, we can estimate the distance from the interface in which the sub-100 fs CT would still occur. Previously, we have used this method to study the transport mechanism and the delocalization size of excitons in organic thin films.^{40,56} For an ultrathin (0.5 nm) ZnPc layer, the S₁ peak intensity shows an ultrafast decay in both ZnPc/ML-MoS₂ and ZnPc/bulk MoS₂ samples. By fitting the data to a single exponential decay convoluted with the laser pulse widths (Fig. 3a and b, dashed lines), we found that the ZnPc's S₁ exciton has lifetimes of 40 fs and 55 fs for ZnPc/ML-MoS₂ and ZnPc/bulk MoS₂ respectively, which are attributed to the CT times.

As the ZnPc thickness is increased to 1 ~ 2 nm, the S₁ peak intensity starts to show a slower decay for the bulk-MoS₂ sample (Fig. 3b). By contrast, the decay dynamics is independent of thickness (in the range of 0.5 – 2 nm) for the ML-MoS₂ samples (Fig. 3a). Eventually, when the ZnPc thickness is beyond 4 nm, the S₁ exciton shows a much slower and thickness-independent decay for both samples. Thicker samples show a much slower decay because S₁ excitons near the ZnPc surface need to transport to the interface *via* slow incoherent diffusion before the interfacial

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3 CT can occur.^{24,50} However, if the average thickness of the film is roughly equal to or less than the
4 delocalization size of the S_1 exciton in the ZnPc film, fast population quenching due to the coherent
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6 CT can still be observed. The results in Fig. 3a and 3b imply that the S_1 exciton in the ZnPc film
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8 deposited on the bulk-MoS₂ has a smaller delocalization size because the ultrafast quenching can
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10 no longer be observed in samples with a ZnPc layer as thin as 2 nm. The difference in the
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12 delocalization size can be correlated to the amount of band bending found in the UPS measurement
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14 (Fig. 1d). For the ZnPc/bulk-MoS₂, the amount of the band bending (~ 0.6 eV) is larger than the
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16 electronic coupling between neighboring phthalocyanine molecules (~ 0.1 eV).^{57,58} This uneven
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18 energy landscape would limit the coherent size of the S_1 exciton. Moreover, the direction of the
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20 electric field associated with the band bending pushes the electron away from the interface. These
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22 key differences between the two interfaces are summarized schematically in Fig. 3d. For
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24 ZnPc/bulk-MoS₂, a S_1 exciton slightly farther away from the interface can no longer transfer its
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26 electron coherently to the MoS₂. On the other hand, the lesser band bending in ZnPc on ML-MoS₂
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28 results in the larger delocalization size of the S_1 exciton, which can enable coherent CT even
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30 though the exciton is farther away from the interface. For practical applications, this larger
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32 coherent CT range is important because it will allow the interface to dissociate a larger amount of
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34 S_1 excitons on the sub-ps timescale.
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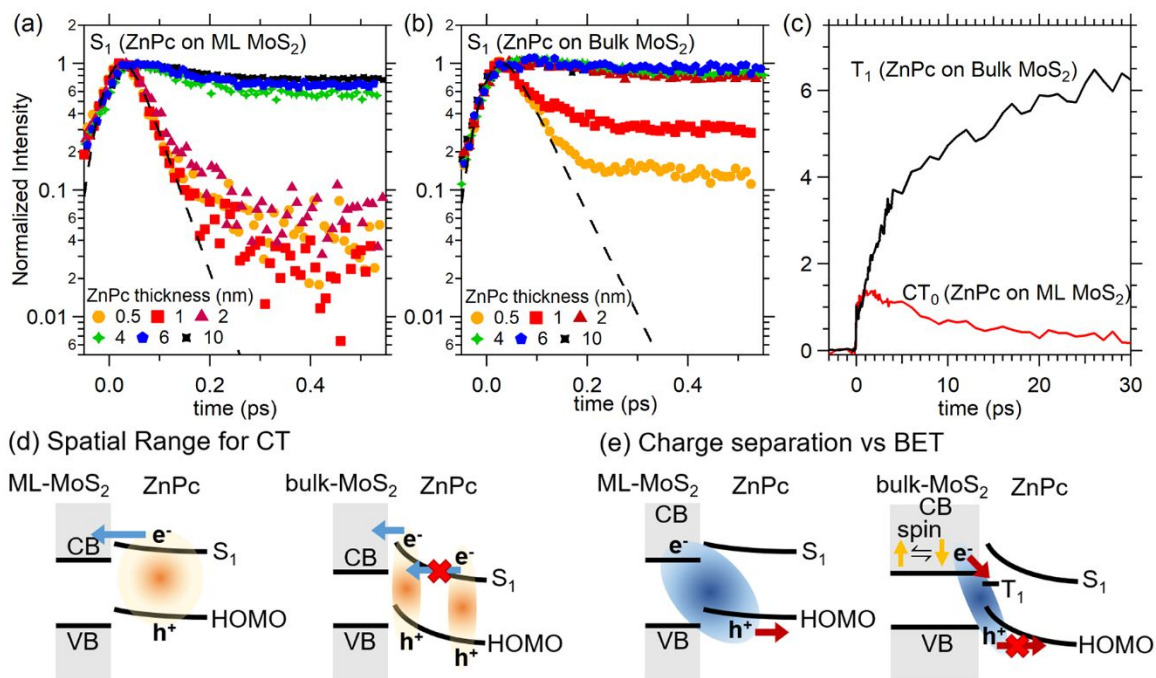


Figure 3: The S_1 peak intensity as a function of time for samples with various ZnPc thicknesses. Panel (a) and (b) show the results from the ML and bulk MoS_2 respectively. The dashed lines show the fit to an exponential decay. (c) The temporal evolution of the intensity for the CT_0 and T_1 states in the 1 nm ZnPc/ML- MoS_2 and the 1 nm ZnPc/bulk- MoS_2 samples respectively. (d) A schematic diagram shows that a large band bending in ZnPc on bulk MoS_2 can limit the extent of exciton delocalization and prohibit electron injection. These two factors limit the spatial range of the coherent CT. (e) Large band bending in ZnPc on bulk MoS_2 can trap the hole of the CT exciton near the interface. The hole trapping together with the faster spin flipping rate in bulk- MoS_2 favor back electron transfer (BET) and T_1 formation at the ZnPc/bulk- MoS_2 interface.

Competition between Back Electron Transfer and Exciton Dissociation

After the initial CT process, the CT exciton formed at the interface needs to be dissociated in order to generate free carriers. However, other electronic processes can compete with the dissociation of the CT exciton. Indeed, for bulk- MoS_2 /ZnPc, we have reported that triplet (T_1) exciton can be formed in the ZnPc film *via* spin-flipping in MoS_2 and subsequent back electron transfer (BET) from bulk- MoS_2 to ZnPc.²⁴ For ZnPc/bulk- MoS_2 , the population of the T_1 exciton was found to increase on the 10 – 100 ps timescales. The T_1 formation kinetics for 1 nm-ZnPc/bulk- MoS_2 is reproduced in Fig. 3c (the black curve). The spectral signature of the T_1 exciton is rather distinctive in the TPPE spectrum²⁴ because the signal intensity is larger compared to other states

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3 and it has a very long lifetime. However, such a T_1 state is not observed for the ZnPc/ML-MoS₂
4 interface. The longest-lived state identifiable in the 1 nm ZnPc/ML-MoS₂ spectrum (Fig. 2) is the
5 CT₀ state. For comparison, the intensity evolution of this state is shown in Fig. 3c (red curve).
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7 After the intensity is peaked at ~ 1 ps, it decreases monotonically with time. Hence, we do not
8 observe the signature for the BET and T_1 formation at the ZnPc/ML-MoS₂ interface.
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14 For the ZnPc/bulk-MoS₂ interface, two factors that favor the T_1 formation can be identified.
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16 First, the spin lifetime is supposed to be longer in ML-MoS₂ as compared to bulk-MoS₂ because
17 of the spin-momentum locking in ML-MoS₂.^{31,32} Indeed, recent works on ML-TMDC
18 heterostructures have shown that CT excitons in these heterostructures can have a very long spin
19 lifetime.⁵⁹ Second, the large band bending in the ZnPc film on bulk-MoS₂ can essentially trap the
20 hole of the CT exciton very close to the interface (Fig. 3e). The close proximity of the hole in ZnPc
21 to the electron in MoS₂ can increase the chance of the BET. Indeed, the exchange interaction that
22 provides the energetic driving force for the T_1 formation is a very short range interaction (within
23 the size of a molecule). Hence, hole trapping at the interface would be a crucial step for T_1
24 formation *via* the BET. We note that band bending has also been invoked recently to explain the
25 triplet formation at the CuPc/GaAs interface.⁶⁰
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40 We do not observe significant T_1 formation at ZnPc/ML-MoS₂. Instead, the CT₀ intensity
41 is found to decay on the order of 10s of ps (Fig. 3c). The disappearance of the CT₀ state can be
42 explained by two different scenarios. In the first scenario, the interfacial CT exciton simply
43 recombines at the interface. However, this seems to be unlikely because a number of recent time-
44 resolved studies found that the CT states or separated carriers in similar organic-TMDC interfaces
45 have much longer lifetimes.^{23,25,26} In the second scenario, the localized CT exciton dissociates into
46 an electron-hole pair with the hole in ZnPc and the electron in MoS₂. However, the signal
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3 disappears because our TR-TPPE probe is not sensitive to both delocalized electrons in MoS₂ and
4 holes in ZnPc. The TR-TPPE cannot probe the hole in ZnPc because it can only measure excited
5 electrons. For separated electrons in ML-MoS₂, they are resided at K valleys in the momentum
6 space, which has a large in-plane momentum. To detect these electrons, momentum conservation
7 will need to be fulfilled in the photoionization process⁶¹ (the probe process) and a probe photon
8 energy of $\sim 10 - 20$ eV is required.^{54,55} Our probe photons only have an energy of 4.68 eV, which
9 is not enough to ionize electrons in the K valleys through a direct optical process. As a result, our
10 probe is not sensitive to the separated electrons in MoS₂. Indeed, our control experiments on bare
11 ML-MoS₂ (supporting information) shows that the TPPE signal is an order of magnitude weaker
12 compared to the ZnPc/MoS₂ samples even when the ML-MoS₂ is excited resonantly at ≈ 1.88 eV.
13 Similarly, in bare bulk-MoS₂, the primary photo-excited species is free electron and no TPPE
14 signal can be observed.²⁴ These control experiments shows that our TPPE probe cannot detect
15 free electrons at the K valleys in MoS₂. Therefore, the gradual decrease in the CT₀ intensity can
16 be explained by the dissociation of localized CT excitons (which do not have a well-defined k -
17 vector) into delocalized electrons in the ML-MoS₂ with a well-defined momentum.
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38 To distinguish the above two scenarios, another time-resolved probe is used to detect long-
39 lived excited states that may have been missed out by the TR-TPPE experiment. Transient
40 absorption measurement is done on the 2 nm ZnPc/ML-MoS₂ sample to find out whether long-
41 lived states exist. In this experiment, the sample is pumped at 710 nm (1.75 eV, similar to the
42 pump wavelength used in the TPPE experiment) and the transient change in reflectance at 420 nm
43 is measured. As mentioned above, the pump photons selectively excite ZnPc and no significant
44 signal is observed in the bare ML-MoS₂ sample (Supporting information, Fig. S7). The choice of
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wavelength of 660 nm (which can probe the A-exciton bleaching in MoS₂ directly) because it would be too close to the pump wavelength. Nevertheless, this probe wavelength (420 nm) can detect excitation in both ZnPc and MoS₂. In Fig. 4, the transient change in the reflectance ($\Delta R/R$) for the ZnPc/ML-MoS₂ sample is shown (solid square), which is compared to the data obtained from a 10 nm ZnPc/SiO₂/Si sample (open circle). For comparison, the signal from the ZnPc-only sample is divided by a factor of 5 to account for its larger thickness. It is clear that the positive signal in both traces is originated from the ZnPc layer, which can be attributed to the photobleaching of the ZnPc's B-band (an increase in R can be resulted from a decrease in absorption). The measured dynamics for the ZnPc-only sample is comparable to the S₁ exciton population in the same sample measured by TR-TPPE (solid line).

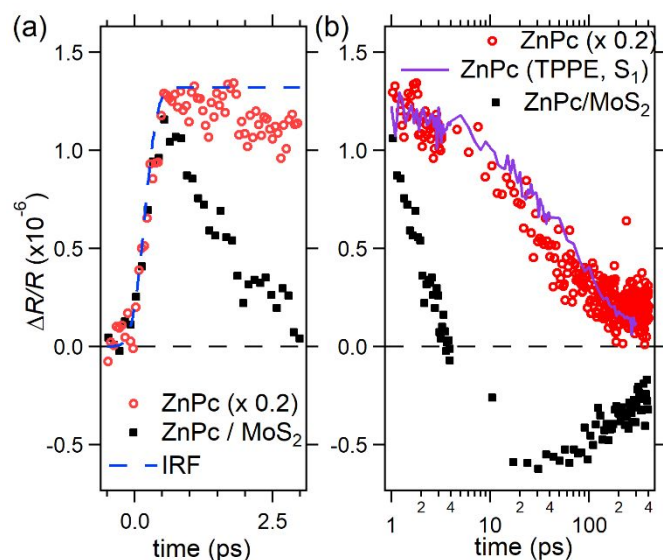


Figure 4: The transient absorption of the 2 nm ZnPc/ML-MoS₂ and 10 nm ZnPc samples measured at 420 nm. The samples are pumped at 710 nm, which selectively excites the ZnPc's S₁ exciton. For comparison, the signal for the ZnPc-only sample is divided by 5 to account for the difference in the ZnPc film thickness. Panel (a) and (b) show the dynamics on two different timescales. In panel (a), the instrumental response function (IRF), which is the integral of a Gaussian function with a fwhm of 400 fs, is indicated by the dashed line. In panel (b), the S₁ peak intensity of the ZnPc-only sample measured by the TR-TPPE experiment (solid line) is shown for comparison.

The initial signal rise overlaps with the instrumental response (~ 400 fs) indicated by the dashed line in Fig. 4a. Hence, the positive signal near time zero is originated from the optically-

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3 excited S_1 exciton in ZnPc. For the ZnPc/ML-MoS₂ sample, the positive signal decreases rapidly
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5 in the first 1 – 2 ps, which is consistent to the annihilation of the S_1 exciton *via* ultrafast CT
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7 discussed above. Then, the signal changes to negative after a few ps, which magnitude decays on
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9 a 100 ps time scale. The decay time of the positive signal is similar to that of the CT₀ population
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11 observed in the TR-TPPE experiment (Fig. 3c). Following the decay of the positive signal, a long-
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13 lived negative signal appears at $t \sim 20$ ps. We attribute the long-lived negative signal to the
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15 population of electrons in ML-MoS₂ resulted from the dissociation of CT excitons. The probe
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17 photon energy is close to the C-exciton resonance of MoS₂.⁶² Hence, the signal originates from the
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19 change of the C-exciton resonance by these electrons. The decay time of several 100 ps is also
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21 consistent with lifetime of electrons in MoS₂ when they are spatially separated from holes by a
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23 vdW interface in TMDC heterobilayers.^{63,64} Unlike excitons, which reduce transient absorption of
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25 exciton resonances mainly by phase space state filling effect and thus produce photobleaching,
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27 electrons as charged particles can alter the exciton resonance effectively by screening effect, which
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29 mainly cause a shift of the resonance. Hence, the sign of the signal (photoinduced absorption or
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31 photobleaching) depends on the direction of the shift. In the measurement, we found the signal to
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33 be negative. Based on both the transient absorption and the TR-TPPE measurements, we conclude
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35 that the CT₀ exciton does not recombine. Instead, they dissociate into free electrons in MoS₂ and
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37 holes in ZnPc.
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45 Compared to typical organic-organic interfaces, the time taken for the dissociation of the
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47 CT exciton at the ZnPc/MoS₂ interface is relatively short (~ 10 ps). For example, bound CT
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49 excitons at the ZnPc/C₆₀ interface dissociate on the ~ 1 ns timescale.^{53,65} The relatively fast CT
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51 exciton dissociation dynamics can be explained by a smaller exciton binding energy. Moreover,
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53 the delocalized nature of electrons in MoS₂ should increase the density of less-localized and
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loosely bound CT states. A larger number of available CT states with small binding energies and large spatial extents should favor the CT exciton dissociation driven by the entropy.⁶⁶⁻⁶⁸

CONCLUSION

A major conclusion that can be drawn from our work is that although the type-II band alignment is necessary for enabling ultrafast interfacial CT, it is not a decisive factor in determining whether free electrons and holes can be generated effectively from the interface. In particular, we demonstrate that the potential energy landscape near the interface, together with the spin lifetime in the TMDC, can govern the spatial range of the coherent interfacial CT process and the subsequent evolution of the CT exciton. Both ZnPc/ML-MoS₂ and ZnPc/bulk-MoS₂ interfaces are found to have a type-II band alignment with a similar MoS₂-VBM/ZnPc-HOMO energy offset at the interface. However, the VBM of bulk-MoS₂ has a higher energy than that of the ML-MoS₂, which results in the much stronger band bending found in the ZnPc film deposited on the bulk-MoS₂. This band bending not only limits the spatial range of the coherent CT, it also determines the eventual fate of CT excitons. For ZnPc/bulk-MoS₂, CT excitons transition into triplet excitons in ZnPc *via* faster spin flipping in bulk-MoS₂ and more effective back electron transfer to ZnPc. We attribute the more effective back electron transfer process to the larger band bending in ZnPc because the hole in ZnPc is likely to be trapped at the interface by the large potential gradient associated with the band bending. By contrast, the flatter band structure at the ZnPc/ML-MoS₂ interface and the longer spin lifetime in ML-MoS₂ favor the dissociation of the CT excitons. The very different exciton dynamics found at the two interfaces shows that the interfacial energy level alignment, by itself, is not a good predictor in determining whether free charges can be generated effectively from these interfaces.

ASSOCIATED CONTENT

Supporting Information

Data on the characterization of the monolayer MoS₂, additional UPS, TR-TPPE and transient absorption data for control experiments.

AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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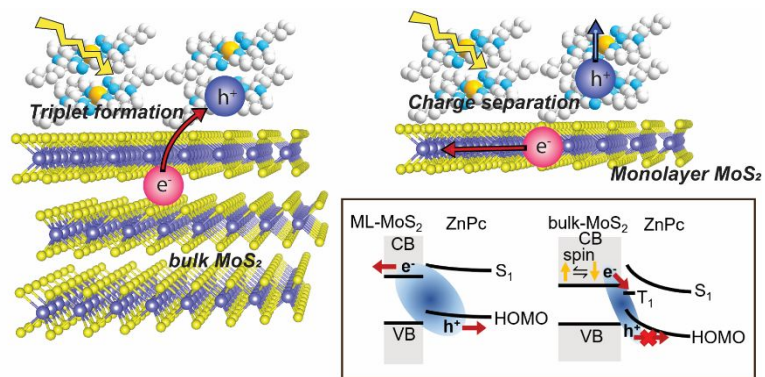
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TOC figure

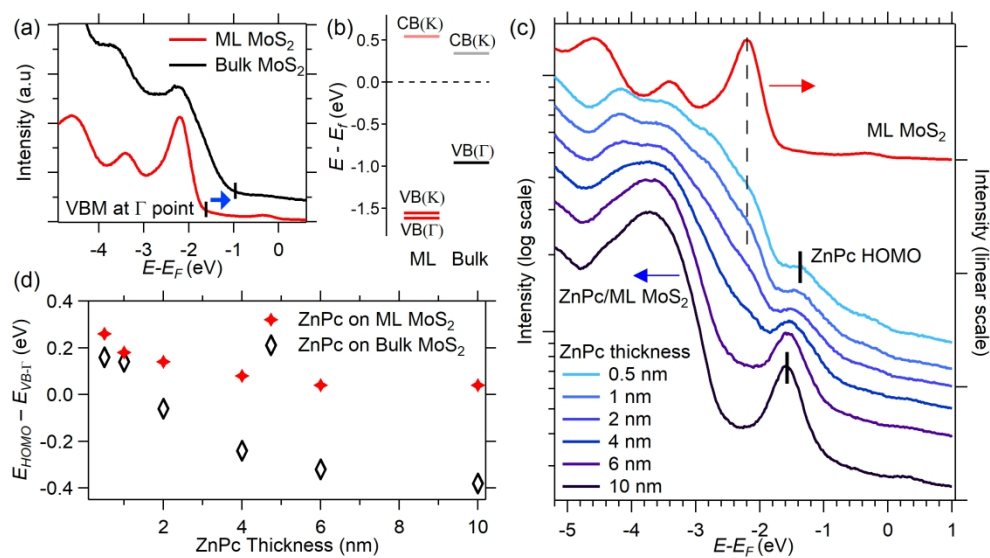


Figure 1

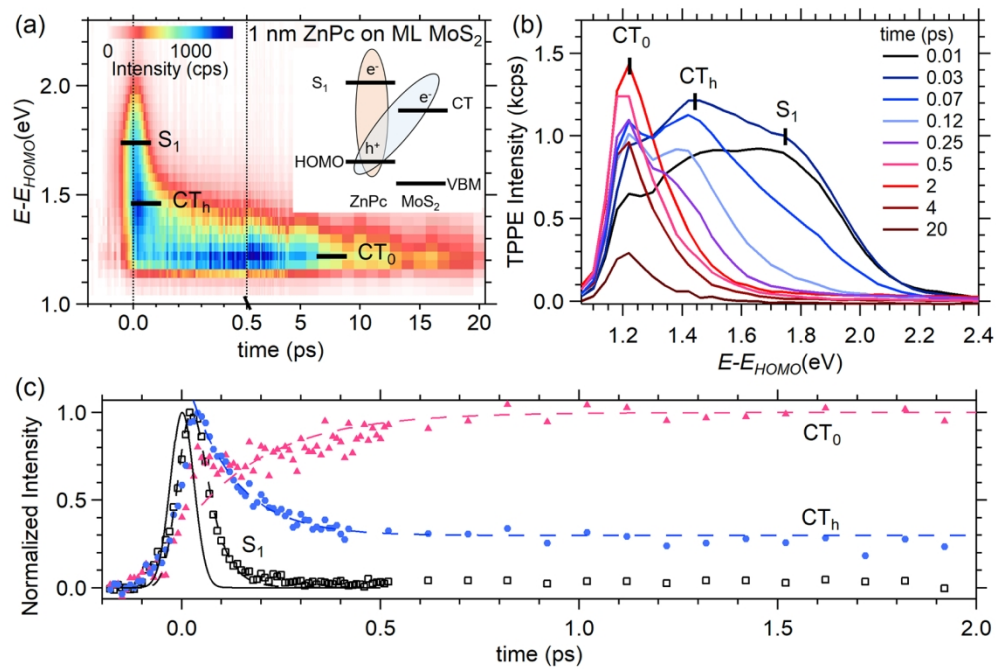


Figure 2

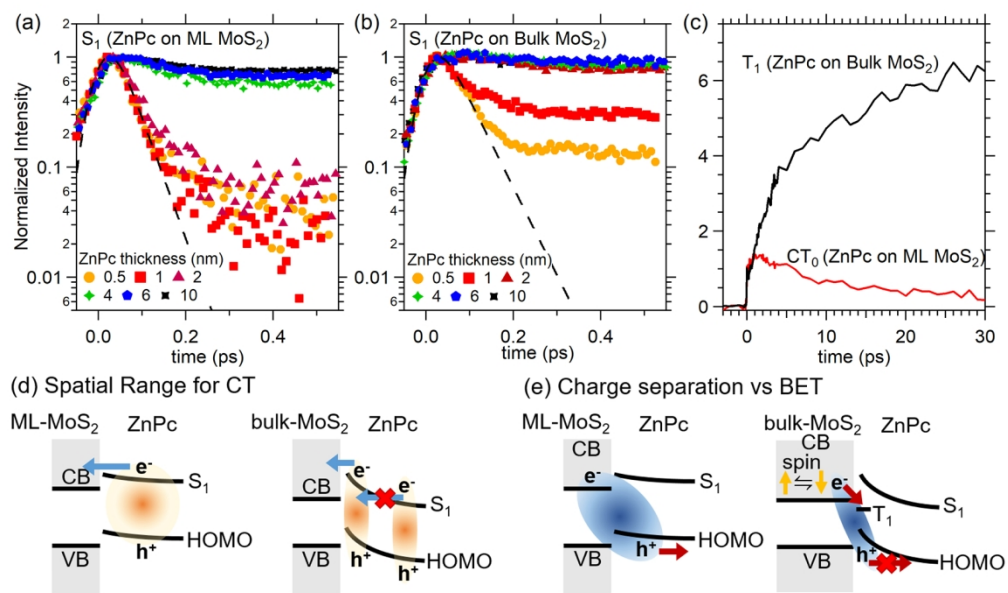


Figure 3

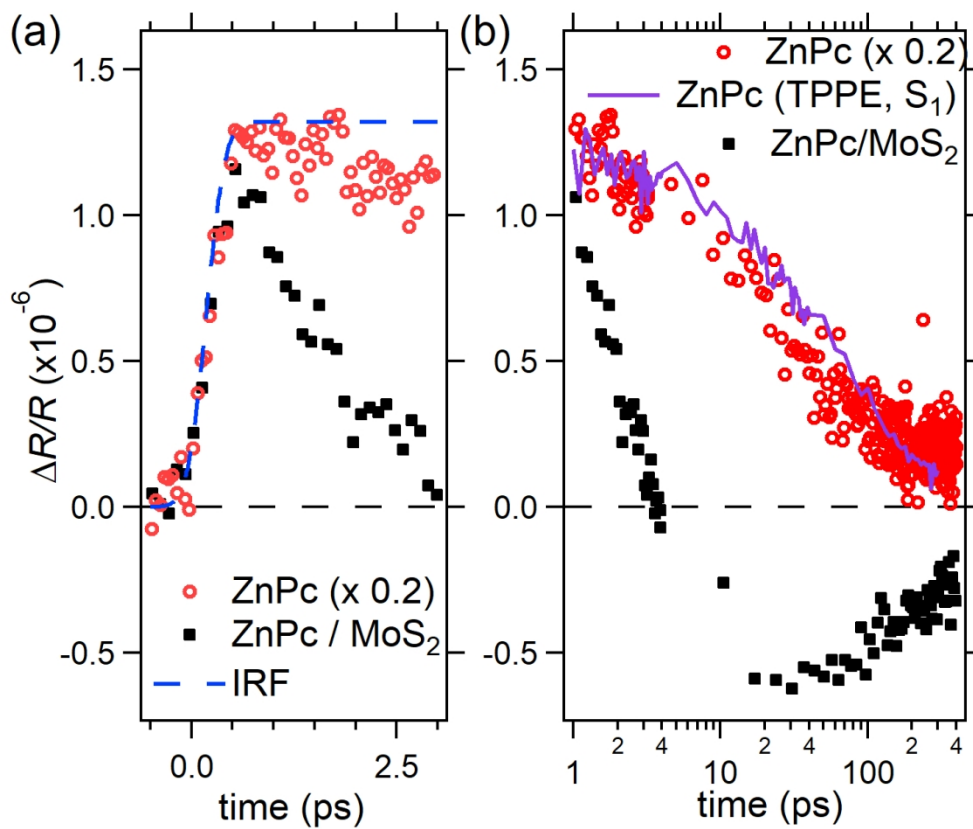
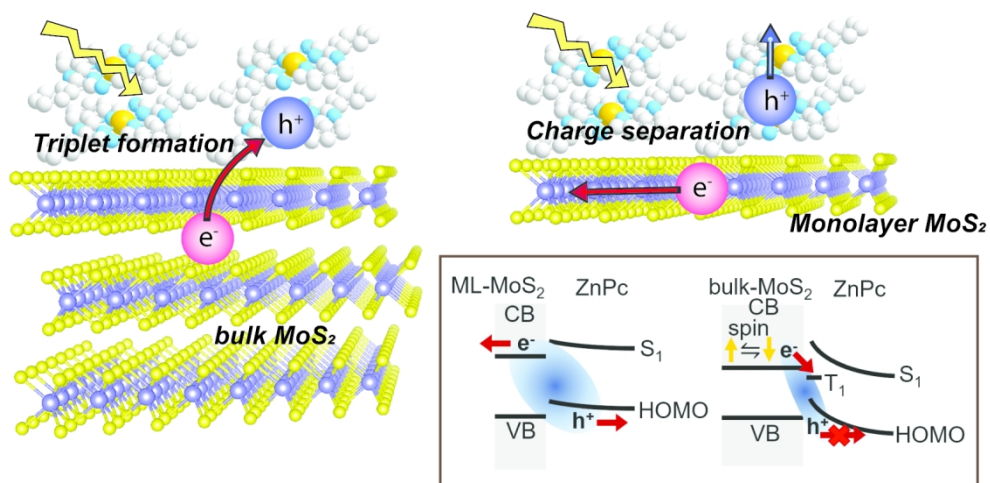


Figure 4



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