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17% Efficient Organic Solar Cells Based on Liquid Exfoliated WS₂ as Replacement to PEDOT:PSS

Yuanbao Lin, Begimai Adilbekova, Yuliar Firdaus, Emre Yengel, Hendrik Faber, Muhammad Sajjad, Xiaopeng Zheng, Emre Yarali, Akmaral Seitkhan, Osman M. Bakr, Abdulrahman El-Labban, Udo Schwingenschlögl, Vincent Tung, Iain McCulloch, Frédéric Laquai, Thomas D. Anthopoulos*

Y. Lin, B. Adilbekova, Y. Firdaus, E. Yengel, H. Faber, M. Sajjad, E. Yarali, G. T. Harrison, A. Seitkhan Dr. A. El-Labban, Prof. U. Schwingenschlögl, Prof. V. Tung, Prof. I. McCulloch, Prof. F. Laquai and Prof. T. D. Anthopoulos King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC), Thuwal 23955, Saudi Arabia. Email: thomas.anthopoulos@kaust.edu.sa

X. Zheng and Prof. O. M. Bakr, King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division (PSE), Thuwal 23955, Saudi Arabia.

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Abstract

Here, we report on the application of liquid-exfoliated two-dimensional (2D) transition metal disulfides (TMDs) as the hole transport layers (HTLs) in nonfullerene (NFA)-based organic solar cells. We show that solution processing of few-layer WS₂ or MoS₂ suspensions directly onto transparent indium tin oxide (ITO) electrodes change their work function without the need for any further treatment. HTLs comprising WS₂ are found to exhibit higher uniformity on ITO than those of MoS₂, and consistently yield solar cells with superior power conversion efficiency (PCE), improved fill-factor (FF), enhanced short-circuit current (J_{SC}), and lower series resistance than devices based on PEDOT:PSS and MoS₂. Cells based on the ternary bulk-heterojunction PBDB-T-2F:Y6:PC₇₁BM with WS₂ as the HTL, exhibit the highest PCE of 17%, with a FF of 78%, open circuit voltage of 0.84 V, and a J_{SC} of 26 mA/cm². Analysis of the cells' optical and current transport characteristics indicate that the enhanced performance is most likely attributed to a combination of favorable photonic structure and reduced bimolecular recombination losses in WS₂-based cells. The achieved PCE is the highest reported to date for organic solar cells comprised of 2D charge transport interlayers and highlights the potential of TMDs as inexpensive HTLs for high-efficiency OPVs.

Organic photovoltaics (OPVs) have received tremendous attention in recent years due to their numerous attributes such as the potential for high power conversion efficiency (PCE), mechanical flexibility, semitransparency, and the promise for large-scale manufacturing via low-cost techniques such as roll-to-roll printing processes. ^[1-2] The performance of OPVs has been steadily increasing over the past few years primarily due to impressive strides in new donor and acceptor materials and to significant innovations in device engineering. ^[3] To date, the record PCE values for bulk heterojunction (BHJ) OPVs exceed 16% for single-junction cells, and over 17% for two-terminal tandem cells. ^[4-6] We have recently estimated that nonfullerene acceptor (NFA)-based BHJ OPVs can potentially reach PCE values in excess of 20% and 25% for single-junction and two-terminal tandem cells, respectively, if certain material and device criteria are met.^[7]

These predictions, besides being encouraging, provide impetus for further focused work not only on the cell's photoactive materials, but also on other key device components where additional performance losses can occur. ^[7] One such component is the carrier-selective charge transport interlayers, used to enhance the extraction of photogenerated carriers from the BHJ. ^[8] An ideal interlayer (n- or p-type) should possess energetics that match those of the BHJ layer, and offering considerable processing versatility to ensure layer uniformity avoiding de-wetting, and pinhole formation. ^[9] To date, there are numerous examples of electron-transporting layers (ETLs), such as ZnO, LiF and poly[9,9-bis(6'-bromohexyl)fluorene-alt-co-1,4-phe-nylene (PFN-Br), that have been successfully employed in OPVs. ^[10-11] Unfortunately, this is not the case for hole-transporting layers (HTL), where progress has been limited with only a handful of materials available at present.^[12-14] Currently, the conjugated polymer poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is the most widely used HTL in OPVs - particularly in standard cell architectures. However, PEDOT:PSS is highly hygroscopic and acidic, which contributes to degradation of the commonly used transparent electrode material indium tin oxide (ITO). ^[13] To address these issues, a variety of alternative HTL materials has been proposed,^[14-15] including transition metal oxides such as V_2O_5 , WO_3 etc.^[16] Unfortunately, the majority of these HTLs rely on vacuum processing and/or complex chemistries that require high-temperature annealing, which in turn makes the overall cell manufacturing more complex and energy-intense.

Two-dimensional (2D) semiconductors represent an alternative class of materials that could potentially combine all-important attributes of an ideal interlayer for OPV applications. ^[17] For example, low-dimensional transition metal disulfides (whose generalized formula is MX₂, where M is a transition metal and X embodies a chalcogenide) such as WS₂ and MoS₂ combine suitable energetics with high carrier mobilities and excellent optical transparency, and have already been used in a variety of devices, including photodetectors, transistors, and fullerene-based OPVs. ^[18-20] Despite their demonstrated potential, however, the majority of MX₂-based HTLs rely on post-deposition treatment such as high-temperature annealing (i.e. 300 °C), exposure to ultraviolet-ozone, and/or chemical doping for work function (WF) tuning.^[19, 21] Besides, controlling the morphology and uniformity of solution-processed MX₂ carrier transporting layers has also proven challenging. Therefore, the development of solution-derived MX₂ and their use as reliable charge transport interlayers in high efficiency organic solar cells is timely.

Different synthetic routes have been demonstrated for the synthesis of 2D nanomaterials, which can be broadly categorized into top-down and bottom-up techniques. ^[22] A few examples from both categories include, micromechanical cleavage, mechanical force-assisted liquid exfoliation, chemical vapor deposition, and wet-chemical syntheses. ^[23-24] Among the top-down approaches, sonication represents the simplest and most commonly used method for the liquid exfoliation of 2D nanosheets from layered bulk crystals. This method is cost-efficient with a high-yield is scalable with large-scale production and does not relies on complex equipment or expensive chemicals. ^[25] Importantly, the exfoliated nanosheets are obtained in the form of

liquid suspensions, which may facilitate their incorporation into functional devices for a broad range of applications.^[26]

Here, we report on the use of liquid exfoliated WS₂ and MoS₂ as HTLs in high-efficiency BHJ organic solar cells. As-derived suspensions containing the MX₂ nanosheets are solution processed directly onto ITO electrodes at room temperature without any post-treatment. We find that the exfoliated flakes of WS₂ are thinner than those of MoS₂ and form more continuous layers when spin-coated. First-principles calculations combined with high-resolution imaging and WF measurements suggest that ITO/WS₂ consists primarily of monolayer/bilayer flakes, whereas in ITO/MoS₂ the presence of multilayer flakes appears to dominate, a prediction supported by atomic force microscopy (AFM) and transmission electron microscopy (TEM) measurements. Use of WS₂ as the HTL in NFA-based OPVs, yields cells with consistently improved PCEs. Device analysis shows that this improved performance is attributed to lower bimolecular recombination losses, as compared to MoS₂ and PEDOT:PSS-based cells. Moreover, the wider applicability of WS₂ HTLs is demonstrated by its application in state-ofthe-art binary (PBDB-T-2F polymer donor with Y6 acceptor (2,2'-((2Z,2'Z)-((12,13-bis(2ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-

e]thieno[2,"30":4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-

diylidene))dimalononitrile)) and ternary (PBDB-T-2F:Y6:[6,6]-phenyl-C71-butyric acid methyl ester) (PC₇₁BM) BHJ OPVs,^[5] for which maximum PCE values of 16. 4% and 17%, are obtained, respectively. These are the highest PCE values reported to date for OPVs based on 2D HTLs and amongst the highest for organic solar cells.

We exfoliated WS₂ and MoS₂ using previously reported protocols.^[27] In brief, a powder of the respective bulk material was added to ethanol:water (1:1 vol.) and sonicated using a sonic probe for 6 h with the temperature of the sample maintained at 5 °C (**Figure 1**a). The resulting suspension was then centrifuged and the supernatant containing the nanoflakes was carefully

extracted. Figure 1b shows the UV-vis absorption spectra of the extracted WS₂ and MoS₂ flakes in ethanol:water, both consistent with previous reports.^[28] Analysis of the 2D nanoflakes via TEM reveals the presence of large (>>100 nm) and highly crystalline WS₂ nanosheets (Figure S1a). Clear evidence of the symmetrical arrangement of the W and S atoms in a hexagonal motif with *d*-spacings of 2.6 Å [(100) planes of WS_2] is provided by the high-resolution TEM images in Figure S1b. Fast Fourier transform (FFT) analysis of the image (inset in Figure S1b) supports the hexagonal symmetry of the atomic arrangement and that the individual sheet consists of a single crystal domain.^[29] On the other hand, TEM analysis of the MoS₂ sample (Figure S1c-d) reveals the presence of analogous nanosheets as WS₂ but with some evidence of multilayers stacking resulting in an ill-defined atomic arrangement in the FFT pattern (inset in Figure S1d). Raman spectroscopy was also used to identify the layer number of WS₂ and MoS₂ nanosheets spin-coated on Si substrate. The typical strong in-plane E_{2g}^{1} and out-of-plane A_{1g} peaks were observed in both samples (Figure S1e-f). The position of these peaks are known to correlate with the thickness of TMDs nanosheets.^[30] For most of the WS₂ nanosheets a frequency difference between ≈ 65 and ≈ 68.5 cm⁻¹ is observed, corresponding to single and bilayer, respectively.^[30b] For most of the MoS₂ nanosheets (Figure S1f), we observed a frequency difference of around ≈ 23 and ≈ 24.4 cm⁻¹, which is again indicative of the presence of bilayer and trilayer nanosheets, respectively.^[30c]

As-prepared MX₂ suspensions were spin-coated onto ITO without any further treatment. We used AFM to study the surface morphologies of the ITO before and after MX₂ deposition (Figure 1d). From the surface topography images it is difficult to observe noticeable differences between the ITO and the ITO/MX₂ due to the conformity and the ultra-thin nature of the MX₂ nanosheets. However, analysis of the height histograms extracted from the AFM images (Figure S2a-d), reveals significant shifts in the distribution towards lower height values, indicating the existence of smoother/flatter ITO surfaces. The MX₂ nanosheets appear to overlay voids and other surface features that are intrinsic characteristics of the rougher ITO surface. Among the two MX₂ systems, ITO/WS₂ is found to exhibit the smoothest surface topography. By spincoating the same MX₂ suspensions on SiO₂ and performing the AFM measurements, we were able to study the size and thickness of the individual nanosheets. Figure S2e-g displays the AFM images of the as-spun nanosheets. WS₂ flakes appear to be larger and thinner than MoS₂. From the height histogram in Figure S2g, we estimated the number of layers for the two materials. WS₂ flakes consist mostly of 2-3 monolayers (max thickness \approx 3 nm), while MoS₂ flakes appear significantly thicker consisting of 2-8 monolayers (max thickness \approx 7.5 nm). Lastly, WS₂ flakes appear to be larger in lateral size than MoS₂, which may be partly responsible for the improved smoothening effect of the ITO surface seen in Figure S2d.

Further evidence of the presence of the MX₂ nanosheets after spin coating on ITO are provided by energy dispersive X-ray spectroscopy (EDX) measurements performed during SEM imaging (coloured images in Figure 1d). WS₂ nanosheets, indicated by the presence of W (EDX: W), appear to fully cover the surface of ITO. This is not the case for MoS₂, where the presence of gaps in the elemental mapping of Mo (EDX: Mo) are observed. The different surface coverage behaviour is most likely attributed to the differences in the shape and size of the exfoliated flakes of WS₂ and MoS₂ (Figure S2e-g) and/or their interaction with the ITO surface.

Next, we examined the impact of the MX₂ HTLs on the surface morphology of the binary BHJ layer (composed of PBDB-T-SF:IT-4F) deposited atop, using AFM. **Figure 2**a-d presents the AFM images for the BHJ layer deposited on: ITO/WS₂, ITO/MoS₂, ITO/PEDOT:PSS and ITO. Both WS₂/BHJ (Figure 2a) and MoS₂/BHJ (Figure 2b) samples exhibit similar surface topographies which are smoother than that of the BHJ deposited on both PEDOT:PSS and ITO (Figure 2c-d). These differences can be distinguished in the surface height histograms of Figure 2e extracted from the AFM images. Evidently, WS₂/BHJ exhibits the smoothest surface with a surface root-mean-square (rms) roughness of 1.24 nm, followed by the MoS₂/BHJ (1.42 nm), the PEDOT:PSS/BHJ (2.38 nm) and the ITO/BHJ (2.79 nm). These differences are most likely

caused by the different surface energies of the HTLs and/or substrate, an important parameter known to influence the morphology of the BHJ layer.^[31] In an effort to quantify the surface energy differences, we performed contact-angle measurements for each HTL material, from which the different surface energy components were inferred using Owens equation (see Table S2 in *Supporting Information*). ^[32] ITO/WS₂ (71.5 mN/m) and ITO/MoS₂ (70.7 mN/m) exhibit surface energy values that are higher than both bare ITO (58.8 mN/m) and ITO/PEDOT:PSS (58.3 mN/m). Interestingly, we find that significant changes in the surface energy and contact angle of ITO may also be achieved by spin-casting the ethanol:water solvent alone. Figure S3 and Table S3 shows how spin-casting of the solvent mixture onto ITO causes significant change in the surface energetics of ITO. In the case of OPVs we suspect that the difference in surface energetics between the samples may account for the variation of the BHJ topography seen in Figure 2e.^[8]

We performed Kevin probe measurements to determine the WF of ITO before and after deposition of the HTLs. As shown in Figure 2f, the WF of WS₂ and MoS₂ deposited on ITO are very similar and equal to -5.5 and -5.4 eV, respectively. The shallower WF of MoS₂ is most likely the result of the present of multilayer flakes present on the surface of ITO in agreement with the AFM analysis (Figure S2g). Importantly, both values are significantly lower than that of the UV-treated ITO (-4.7 eV) and ITO/PEDOT:PSS (-4.8 eV) (Table S3). This is an interesting finding and demonstrates the ability of solution-processed MX₂ nanosheets to alter the WF of the ITO electrode. The significant WF shift is expected to lead to the formation of a better hole extracting contact with the BHJ layer as compared to PEDOT:PSS.^[33]

In an effort to determine the average number of layers in the 2D MX₂ HTL, we use the Vienna Ab-initio Simulation Package to perform first-principles calculations, based on density functional theory, for bare ITO and the monolayer, bilayer, and trilayer MoS₂ and WS₂. We calculated the WF as the difference between the vacuum energy (E_V) and the Fermi energy (E_F) as shown in Figure S4. As can be seen in Table S3 and Figure 2f, the calculated WF for ITO (-

4.7 eV) is in agreement with our experimental value. Furthermore, the calculations show that the WF increases from -5.7 to -5.2 eV for WS₂ and from -5.9 to -5.4 eV for MoS₂, when the number of sheets increases from monolayer to trilayer. These findings, combined with the aforementioned experimental results, suggest that the as-spun nanosheets tend to form primarily 1-3 monolayer HTLs for the case of WS₂ and multilayers (\geq 3) for the MoS₂.

Next we investigated the potential of the liquid-exfoliated MoS_2 and WS_2 as HTLs in OPVs. We fabricated standard structure BHJ cells (Figure 3a) using the PBDB-T-SF polymer as the electron donor and the small-molecule IT-4F as the NFA material (Figure 3b).^[34] We also analysed control cells comprising PEDOT:PSS as the HTL and fully characterized them in parallel. First, we investigated the effect of processing parameters on the cells' performance such as centrifuge speed and spin speed used during exfoliation and deposition of the MX₂ suspensions (Figure S5). Tables S4 and S5 summarize the materials preparation (centrifugation speed), and deposition (spin-coating speed) conditions and the corresponding cells' parameters, while Figure 3c and **Table 1** present representative *J*-*V* for the best performing cells. Devices based on PEDOT:PSS exhibited a maximum PCE value of 13.1% with a short-circuit current density (J_{SC}) of 20.2 mA/cm², an open circuit voltage (V_{OC}) of 0.90 V, a fill factor (FF) of 0.72, and a series resistance (R_S) of 3.7 Ω cm². When PEDOT:PSS was replaced by WS₂ as the HTL, the PCE increased to an increased value of 13.5%. This increase was accompanied by a reduced R_s (3.4 Ω cm²), an increased J_{sc} (20.6 mA/cm²), an improved FF (0.74), and a slightly reduced V_{OC} (0.88 V). When WS₂ was replaced by MoS₂ as the HTL, the PCE reduced to 12% primarily due to the reduced V_{OC} (0.84 V) and J_{SC} (20 mA/cm²), and at least partly, to the increased Rs (4.1 Ω cm²). The noticeable V_{OC} loss of 0.06 V is likely a direct consequence of the shallower WF of the MoS₂ flakes (Figure 2f) and/or the lower surface coverage of ITO by the MoS₂ nanosheets (Figure 1d). The latter effect is expected to result to increased charge recombination and current leakage at the HTL/BHJ interface. Supporting evidence for this hypothesis come from bare ITO-based OPV cells which yield the lowest values for V_{OC} (0.61 V), FF (0.63), J_{SC}

(15.26 mA/cm²) and PCE (5.8%). The bare ITO-based cell defines the lower limit of achievable performance for this particular BHJ systems due to significant recombination of photogenerated carriers at the ITO/BHJ interface. A similar conclusion can be extracted from the MX₂ preparation conditions and corresponding cell performance summarized in Tables S4 and S5. These data suggests that when the concentration/thickness of the nanoflakes/HTL reduces, all cell parameters degrade (Figure S5), resembling more those of the bare ITO-based cells. On the basis of these data we conclude that the size/shape of the flakes and the resulting coverage of the ITO electrode by the 2D-based HTL are critical parameters that need to be taken into consideration for achieving optimal device performance.

Figure 3d displays the external quantum efficiency (EQE) spectra of the PBDB-T-SF:IT-4F cells incorporating the various HTLs. For all devices, the integral current density values deduced from the EQE spectra are well matched with the values obtained from the J-Vmeasurements within 4%. Both WS₂ and MoS₂-based cells showed similar photoresponses between 350 to 550 nm, which is significantly different from that of PEDOT:PSS-based devices. The difference in EQE between the 2D MX₂ and PEDOT:PSS-based cells corresponds to the characteristic variation in device reflectance spectra and absorption of HTLs on ITO as shown in Figure S6. Optical simulations based on transfer matrix formalism show that due to the difference in the layer stack, OPV devices without the PEDOT:PSS spacer layer exhibit slightly higher intensity of electric field and exciton generation rate in the active layer (Figure S7). Interestingly, WS₂-based cells exhibit higher EQE from 600 to 800 nm than the other two types of devices, subsequently leading to a larger J_{SC} . Figure 2d also overlays the internal quantum efficiency (IQE) spectra, which decouples the effect of optical absorption. The average IQEs of cells with WS₂ is 84.7% in the range 350-800 nm, with its maximum value reaching 98.5% at 460 nm. In comparison, the average IQEs for cells with PEDOT:PSS and MoS₂ are close to 81.9% and 82.2%, respectively. The higher average IQEs of the WS₂ cells suggest that a larger portion of the absorbed photons are converted to free carriers that are then successfully collected

by the electrodes. The observed losses seen at the IQE spectra for MoS₂ and PEDOT:PSS cells may stem from higher charge-carrier recombination during transport and will be discussed later.

We investigated the impact of HTLs on charge-carrier recombination in all OPV cells via light intensity dependence J-V measurements (Figure S8). Figure 3e shows the variation of V_{OC} *vs.* light intensity on a logarithmic scale with data fitted to $V_{OC} \propto nkT/q \ln(I)$, where k, T, and q are the Boltzmann constant, the temperature in K, and the elementary charge, respectively. The parameter *n* (usually > 1) reflects the presence/absence of carrier traps across the active layers or at interfaces with electrodes. If trap-assisted recombination is involved, a stronger dependence of V_{OC} on the light intensity with a slope greater than kT/q will be observed. ^[35] The dependence of V_{OC} on the light intensity for the WS₂-based device presents a slope of 1.19 kT/q, which is much lower than 1.58 kT/q for the MoS₂-based device and is slightly higher than 1.06 kT/q for conventional PEDOT:PSS-based cells. Although the higher n for the MoS₂-based cells suggest more severe trap-assisted recombination, the number can be misleadingly inflated due to the higher leakage current.^[36] We then analysed the dark J-V characteristics of the OPV cells in an effort to elucidate the origin of the differences in the devices' performance (Figure S9). Cells based on PEDOT:PSS and WS₂ as the HTLs show similar reverse currents in the voltage range of -1 to 0 V. However, WS₂-based cells interestingly exhibited slightly higher forward currents (implying a lower junction resistance) between 0 to 0.4 V, which could be related to the higher FF and J_{SC} measured for WS₂-based OPVs. MoS₂-based cells, on the other hand, exhibited noticeably higher leakage currents both under reverse and forward bias, explaining the reduced V_{OC} , in line with previous reports. ^[37] This indicates that although the work function of MoS₂ is similar to WS₂, the non-uniform/continuous nature of the MoS₂ layer deposited on ITO (see EDX data in Figure 1d) reduce the charge selectivity of the HTL and increase the leakage current due to minority carrier recombination.

We also examined the light-intensity dependence of J_{SC} to estimate the bimolecular recombination losses in each type of cell (Figure 3f). The relationship between J_{SC} and incident

light intensity (P_{light}) can be described as $J_{SC} \propto (P_{light})^S$. Here, *S* should be equal to 1 if all dissociated free carriers are collected at the corresponding electrodes without any recombination, whereas S < 1 indicates the presence of bimolecular recombination to some extent.^[38] For OPV cells with WS₂ HTL, an *S* value of 1 is obtained, compared to 0.94 and 0.97 for devices with MoS₂ and PEDOT:PSS, respectively. This indicates that WS₂ can sweep out charge carriers more efficiently with negligible bimolecular recombination compared to cells based on other HTL systems. In parallel, the dependence of J_{SC}/J_{sat} on light intensity (Figure 3g), where J_{sat} is the saturation current measured at -3 V, also points to negligible bimolecular recombination losses are not apparent when considering the relative independence of J_{SC}/J_{sat} on P_{light} . Additionally, the 5.8% photocurrent loss inferred from prior examinations of WS₂-based cells may arguably stem from monomolecular recombination processes (e.g. trap-assisted or geminate recombination).^[39] The photocurrent losses gradually increase to 14.7% and 10% for MoS₂ and PEDOT:PSS based devices, respectively, which points to more significant monomolecular recombination in those cells.

Further insights into charge recombination across the device with respect to the HTL employed, can be inferred from transient-photovoltage (TPV) and charge extraction (CE) measurements. We extracted The carrier lifetime (τ) presented in Figure S8d from the TPV decay dynamics using mono-exponential fits for a broad range of light intensities (3-100% of the maximum light intensity of 200 mW/cm²).^[39] Figure S8d shows that the devices with WS₂ possess slightly higher τ values (\approx 3 µs) at 100 mW/cm². Here we note that when comparing τ , it is important to estimate the corresponding carrier densities in parallel. To this end, we performed charge-extraction (CE) measurements on the same devices at various light intensities from which the carrier densities were inferred. As shown in Figure S8e, the carrier density decreases upon changing from WS₂, to PEDOT:PSS and to MoS₂-based cells for the same light intensity. This tendency is also in agreement with the *J*_{SC} values extracted from the *J*–*V* curves.

Furthermore, the slightly higher τ values in the aforementioned devices and the higher carrier densities in cells with WS₂ compared to those of devices with MoS₂ and PEDOT:PSS HTL indicate that lower carrier recombination rates prevail in the WS₂-based OPV cells. According to $k_{rec} = 1/(\lambda+1)n\tau$, we then inferred the bimolecular recombination rate constants (k_{rec}) from the carrier lifetime and densities, where λ is the recombination order determined from the analyses presented in Figure S8f. As shown in Figure 3h, at all given carrier densities, k_{rec} for the WS₂-based device is substantially smaller than that of the MoS₂ and PEDOT-PSS-based cells. The lower bimolecular recombination in WS₂-based devices could be attributed to several factors including the deeper WF which enables improved charge collection, and/or the reduced surface energy that led to improved phase separation. Further experimental evidence of the reduced ability of MoS₂ to block minority carriers, are obtained by the dark *J-V* characteristics of OPVs cells based on PBDB-T-SF:IT-4F (Figure S9). Evidently, the MoS₂-based devices exhibit significantly higher current density in both reverse and forward bias directions.

The known similarity in the mobility values for electrons and holes in PBDT-SF:IT-4F blend,^[34] allows use of the photo-CELIV (charge extraction by linearly increasing voltage) technique to obtain the average mobility of both charge carriers in OPV cells incorporating the different HTLs.^[40] Figure S10a-c show the experimentally obtained photo-CELIV transients at different light intensities. The corresponding mobilities are plotted in Figure S10d and were calculated using^{40b}

$$\mu = 2d^2 / (3At^2_{\max}(1 + 0.36\Delta j/j_0)) \tag{1}$$

where *d* is thickness, *A* is the voltage rise speed of the applied voltage pulse, t_{max} is the time to reach the extraction current maximum, Δj and j_0 is a shifting and initial current step, respectively. Evidently, OPV cells with WS₂ exhibit the highest carrier mobility value of 3.3×10^{-4} cm² V⁻¹s⁻¹ (light intensity = 100%), followed by 2.8×10^{-4} cm² V⁻¹s⁻¹ for PEDOT:PSS and 0.8×10^{-4} cm² V⁻¹s⁻¹ for MoS₂ cells, respectively. The observed mobility trend correlates with the aforementioned bimolecular recombination results.

Finally, we investigated the broader applicability of the solution-processed WS₂ HTLs in other state-of-the-art BHJ systems. For this purpose, we investigated two additional blends composed of PBDB-T-2F:Y6 and PBDB-T-2F:Y6:PC₇₁BM (**Figure 4**a).^[5] Figure S11 and Tables S6 summarize the different weight ratio (wt%) for optimizing PBDB-T-2F:Y6:PC₇₁BM system, while **Table 2** presents representative *J-V* for the best performing cells. Evidently, the introduction of WS₂ as the HTL yields cells with consistently enhanced photovoltaic performance compared to control PEDOT:PSS-based cells. We attribute the enhanced PCE to lower *Rs* and the improved *J*_{SC} and FF, in good agreement with the aforementioned findings for PBDB-T-SF:IT-4F-based cells. Specifically, PBDB-T-2F:Y6:PC₇₁BM-based cells yield a maximum PCE of 17. 0%. This value is among the highest efficiencies reported to date for NFA-based single junction solar cells and the highest for OPV cells comprising 2D materials as interfacial layers (**Figure 4**c).^[19, 41-44]

The EQE spectra for both the binary PBDB-T-2F:Y6 and the ternary PBDB-T-2F:Y6:PC₇₁BM cells are displayed in Figure 4d and 4e, respectively. For both BHJs, we observed the major differences in the EQE spectra between WS₂ and PEDOT:PSS in the range 350 to 550 nm, which arises from variation in the device's reflectance (Figure S12). Additionally, WS₂-based cells show a higher EQE beyond 600 nm when compared to conventional PEDOT:PSS-based devices for both BHJ systems. These results are in agreement with those of PBDB-T-SF:IT-4F (Figure 3d). Moreover, the average IQEs of OPVs with WS₂ HTL in the range 350-850 nm are equal to 89. 7% and 91. 7% for PBDB-T-2F:Y6 and PBDB-T-2F:Y6:PC₇₁BM, respectively, whereas for cells with PEDOT:PSS the corresponding values are 87.4 and 87. 4%. For the PBDB-T-2F:Y6 and PBDB-T-2F:Y6:PC₇₁BM the highest values of IQE are obtained at 550 nm (98.2%) and 435 nm (98.1%), respectively, clearly reflecting the high efficiency of these BHJ systems.

In summary, we demonstrated the use of liquid exfoliated WS_2 and MoS_2 nanosheets as solution-processed HTLs in highly efficient NFA-based organic solar cells. We found that direct deposition of MX₂ suspensions on ITO increased its work function significantly more than PEDOT:PSS. Elemental mapping of the ITO/MX₂ electrodes revealed that as-spun WS₂ yields better coverage of the ITO electrode than MoS₂. First-principles calculations of the MX₂ suggest that the processed WS₂ HTLs were composed primarily of a few layer flakes (1-3 monolayers), whereas MoS₂ was composed of multilayer flakes (2-7 monolayers). Solar cells based on PBDB-T-SF:IT-4F BHJ and WS₂ as the HTL yielded a maximum PCE of 13.5%; a significantly higher value than control cells based on PEDOT:PSS (13.1%). Analysis of the carrier recombination processes suggests that the enhanced performance was due to improved charge extraction. By combining WS₂ HTLs with best-in-class binary (PBDB-T-2F:Y6) and ternary (PBDB-T-2F:Y6:PC₇₁BM) BHJ systems, we were able to demonstrate OPV cells with maximum PCEs of 15.8% and 17%, respectively. These remarkable efficiencies are among the highest reported to date for NFA-based single junction solar cells and the highest for OPV devices based on 2D interfacial layers. The work paves the way to a cost-effective HTL technology for application in 3rd generation OPVs.

Experimental

 MX_2 preparation: We added commercial powders of WS₂ and MoS₂ to ethanol:deionized (DI) water (volume ratio 1:1) solutions with concentrations of 6 mg/ml and 8 mg/ml, respectively. Then the solutions were sonicated using a horn probe sonic tip for 6 h (750 W, 20% amplitude). We carried out the sonication process inside a water bath and maintained the temperature at 5 °C to prevent heating of the suspension. We then subjected the dark-coloured dispersions were centrifugation to remove large aggregates. The centrifugation speed ranged from 4000 to 10000 r.p.m. We then carefully collected the supernatants, presumably containing mono- and few-layer nanosheets of WS₂ and MoS₂, which were then used directly for device fabrication. The optimized, in terms of device performance, concentration of WS₂ is 0.6 mg/ml obtained

with a centrifugation speed of 6000 r.p.m, and 0.8 mg/ml for MoS_2 obtained using a centrifugation speed of 8000 r.p.m.

Density Functional Theory (DFT) calculation: We used the Vienna Ab-initio Simulation Package to perform first-principles calculations, based on DFT, for monolayer, bilayer, and trilayer WS₂ and MoS₂.^[45] We also considered ITO (100) slabs, obtained from In-terminated In₂O₃, doped with 5% Sn at the surfaces. The structure models included a vacuum layer of 18 Å thickness to generate two-dimensional geometries. We set the plane wave cutoff energy to 400 eV and we employed the Perdew-Burke-Ernzerhof flavor of the generalized gradient approximation for the exchange correlation functional. The long range van der Waals interaction was taken into account by means of the Grimme method. We use $10 \times 10 \times 1$, $16 \times$ 16×1 , and $20 \times 20 \times 1$ *k*-meshes for the structure relaxations, self-consistent calculations, and non-self-consistent calculations, respectively. In the structure relaxations, we converged the Hellmann-Feynman forces to 0.01 eV/Å for all atoms. We derived the work function as the difference between the vacuum energy E_V and the Fermi energy E_F (valence band maximum) in Figure S4.

Solar Cell Fabrication: PBDB-T-SF, PBDB-T-2F, Y6, IT-4F, PC₇₁BM, and PFN-Br were purchased from Solarmer Materials Inc. Indium tin oxide (ITO) coated glass substrates (Kintec Company, 10Ω sq.⁻¹) were cleaned by sequential ultrasonication in dilute Extran 300 detergent solution, deionized water, acetone, and isopropyl alcohol for 10 min each. The substrates were then subjected to a UV-ozone treatment step for 10 min. Next, a thin layer (\approx 30 nm) of PEDOT:PSS was spin-coated onto the UV-treated substrates and then dried on a heating plate at 150 °C for 10 min. For the 2D MX₂ devices, the suspension containing the WS₂ or MoS₂ nanosheets was spin-coated at 1500 rpm for 60 s onto the UV-treated substrates. The samples were then transferred into a dry nitrogen glove box (<10 ppm O₂). PBDB-T-SF:IT:4F (ratio 1:1, 14 mg mL⁻¹ in chlorobenzene with 0.5% volume DIO) were then spun at 1800 rpm for 30 s (active-layer thickness 90-100 nm). For PBDBT-2F:Y6 and PBDBT-2F:Y6:PC₇₁BM BHJs, the solution were prepared with ratio 1:1.2, and 1:1:0.2, respectively, with concentration of 16 mg mL⁻¹ in chloroform and added 0.5% (volume) chloronaphthalene. The solutions were then spun to obtain active-layer thickness in the narrow range of 140-150 nm. A layer of 5 nm of PFN-Br as electron-transport layer (ETL) was spun from methanol solution (0.5 mg mL⁻¹) on top of the BHJ layer. Finally, the samples were placed in a thermal evaporator and 100 nm of aluminum was then thermally evaporated at 5×10^{-6} mbar through a 0.1 cm² pixel area shadow mask.

Optical Simulation: Simulations of normalized electric-field intensity ($|\mathbf{E}|^2$), and exciton generation within active-layer were calculated by transfer-matrix optical modelling.^[46] This method calculates the reflection and transmission at each interface and the interference between the incident electric field and the fields reflected from the Ag back electrode as well as attenuation in each layer. The optical constants (refractive index, extinction coefficient) for the active layer were collected by variable angle spectroscopic ellipsometry (VASE).

Device Characterization: UV-vis spectra were recorded on a Cary 5000 instrument in single beam mode in 1 cm quartz cuvettes. *J*–*V* measurements of solar cells were performed in a N₂ filled glove box using a Keithley 2400 source meter and an Oriel Sol3A Class AAA solar simulator calibrated to 1 sun, AM1.5G, with a KG-5 silicon reference cell certified by Newport. External quantum efficiency (EQE) was characterized using an EQE system (PV measurement Inc.). Measurements were performed at zero bias by illuminating the device with monochromatic light supplied from a Xenon arc lamp in combination with a dual-grating monochromator. The number of photons incident on the sample was calculated for each wavelength by using a silicon photodiode calibrated by The National Institute of Standards and Technology (NIST). The internal quantum efficiency (IQE) of each OPV cell was calculated using: IQE(%) = EQE(%)/(100% – Reflectance(%) – Parasitic Absorption(%)). The reflectance spectra were collected with the integrating sphere using the same EQE system while the parasitic absorption spectra were obtained from transfer matrix modelling. A Bruker atomic force microscope (AFM) was used to image the surface of the various layers in tapping mode. Scanning electron microscopy (SEM) measurements were performed using a Zeiss Auriga microscope equipped with in-lens detector.

Light-Intensity Dependence Measurements: Light-intensity dependence measurements were performed with PAIOS instrumentation (Fluxim) (steady-state and transient modes). Transient photo-voltage (TPV) measurements monitor the photovoltage decay upon a small optical perturbation during various constant light-intensity biases and at open-circuit bias condition. Variable light-intensity biases lead to a range of measured V_{OC} values that were used for the analysis. During the measurements a small optical perturbation (<3% of the V_{OC} , so that ΔV_{OC} $<< V_{\rm OC}$) is applied. The subsequent voltage decay is then recorded to directly monitor bimolecular charge carrier recombination. The photovoltage decay kinetics of all devices follow a mono-exponential decay: $\delta V = A \exp(-t/\tau)$, where t is the time and τ is the charge carrier lifetime. The "charge extraction" (CE) technique was used to measure the charge carrier density *n* under open-circuit voltage condition. The device is illuminated and kept in open-circuit mode. After light turn-off, the voltage is switched to zero or taken to short-circuit condition to extract the charges. To obtain the number of extracted charges, the current is integrated. The carrier lifetimes follow a power law relationship with charge density: $\tau = \tau_0 n^{-\lambda}$. The bimolecular recombination constant $k_{\rm rec}$ were then inferred from the carrier lifetimes and densities according to $k_{\rm rec} = 1/(\lambda + 1)/n\tau^2$, where λ is the recombination order.

Raman measurements: Raman spectra were collected by Witec Raman microscope using 532 nm excitation.

Supporting Information

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

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References

- [1] Y. Lin, Y. Jin, S. Dong, W. Zheng, J. Yang, A. Liu, F. Liu, Y. Jiang, T. P. Russell, F. Zhang, F. Huang, L. Hou, *Adv. Energy Mater.* **2018**, 8, 1701942.
- [2] Y. Lin, C. Cai, Y. Zhang, W. Zheng, J. Yang, E. Wang, L. Hou, *J. Mater. Chem. A* **2017**, 5, 4093.
- [3] J. Hou, O. Inganäs, R. H. Friend, F. Gao, *Nat. Mater.* 2018, 17, 119.
- [4] L. Meng, Y. Zhang, X. Wan, C. Li, X. Zhang, Y. Wang, X. Ke, Z. Xiao, L. Ding, R. Xia, H.-L. Yip, Y. Cao, Y. Chen, *Science* 2018, 361, 1904.
- [5] J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu, C. Zhu, H. Peng,
 P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski, Y. Li, Y. Zou, *Joule* 2019, DOI: 10.1016/j.joule.2019.01.004.
- [6] B. Fan, D. Zhang, M. Li, W. Zhong, Z. Zeng, L. Ying, F. Huang, Y. Cao, Sci. China Chem. 2019, DOI: 10.1007/s11426-019-9457-5.
- [7] Y. Firdaus, V. M. Le Corre, J. I. Khan, Z. Kan, F. Laquai, P. M. Beaujuge, T. D. Anthopoulos, *Adv. Sci.* **2019**, 1802028.
- [8] Z. Zheng, Q. Hu, S. Zhang, D. Zhang, J. Wang, S. Xie, R. Wang, Y. Qin, W. Li, L. Hong, N. Liang, F. Liu, Y. Zhang, Z. Wei, Z. Tang, T. P. Russell, J. Hou, H. Zhou, Adv. Mater. 2018, 30, 1801801.
- [9] H. Zhou, Y. Zhang, C. K. Mai, S. D. Collins, T. Q. Nguyen, G. C. Bazan, A. J. Heeger, *Adv. Mater.* **2014**, 26, 780.
- [10] Z. He, C. Zhong, S. Su, M. Xu, H. Wu, Y. Cao, *Nat. Photonics* **2012**, 6, 591.
- [11] C. Sun, Z. Wu, Z. Hu, J. Xiao, W. Zhao, H.-W. Li, Q.-Y. Li, S.-W. Tsang, Y.-X. Xu, K. Zhang, *Ener. Environ. Sci.* **2017**, 10, 1784.
- [12] Y. Sun, C. J. Takacs, S. R. Cowan, J. H. Seo, X. Gong, A. Roy, A. J. Heeger, *Adv. Mater.* **2011**, 23, 2226.
- [13] M. De Jong, L. Van Ijzendoorn, M. De Voigt, *Applied Physics Letters* 2000, 77, 2255.
- [14] N. Wijeyasinghe, A. Regoutz, F. Eisner, T. Du, L. Tsetseris, Y.-H. Lin, H. Faber, P. Pattanasattayavong, J. Li, F. Yan, M. A. McLachlan, D. J. Payne, M. Heeney, T. D. Anthopoulos, *Adv. Funct. Mater.* 2017, 27, 1701818.
- [15] J. R. Manders, S.-W. Tsang, M. J. Hartel, T.-H. Lai, S. Chen, C. M. Amb, J. R. Reynolds, F. So, *Adv. Funct. Mater.* **2013**, 23, 2993.
- [16] X. Yu, T. J. Marks, A. Facchetti, *Nat. Mater.* **2016**, 15, 383.
- [17] C. Tan, X. Cao, X.-J. Wu, Q. He, J. Yang, X. Zhang, J. Chen, W. Zhao, S. Han, G.-H. Nam, *Chem. Rev.* 2017, 117, 6225.

- [18] a) N. Huo, G. Konstantatos, *Adv. Mater.* 2018, 30, 1801164. b) S. Lin, S. Liu, Z. Yang, Y. Li, T. W. Ng, Z. Xu, Q. Bao, J. Hao, C. S. Lee, C. Surya, *Adv. Funct. Mater.* 2016, 26, 864.
- [19] K. C. Kwon, C. Kim, Q. V. Le, S. Gim, J.-M. Jeon, J. Y. Ham, J.-L. Lee, H. W. Jang, S. Y. Kim, ACS Nano 2015, 9, 4146.
- [20] G. Tang, P. You, Q. Tai, A. Yang, J. Cao, F. Zheng, Z. Zhou, J. Zhao, P. K. L. Chan, F. Yan, Adv. Mater. 1807689.
- [21] X. Yang, W. Fu, W. Liu, J. Hong, Y. Cai, C. Jin, M. Xu, H. Wang, D. Yang, H. Chen, *J. Mater. Chem. A* **2014**, 2, 7727.
- [22] R. Dong, T. Zhang, X. Feng, *Chem. Rev.* **2018**, 118, 6189.
- [23] V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano, J. N. Coleman, *Science* 2013, 340, 1226419.
- [24] Z. Zeng, C. Tan, X. Huang, S. Bao, H. Zhang, *Ener. Environ. Sci.* 2014, 7, 797.
- [25] K. G. Zhou, N. N. Mao, H. X. Wang, Y. Peng, H. L. Zhang, Angew. Chem. Int. Edit. 2011, 50, 10839.
- [26] Q. Yang, Y. Su, C. Chi, C. Cherian, K. Huang, V. Kravets, F. Wang, J. Zhang, A. Pratt, A. Grigorenko, *Nat. Mater.* **2017**, 16, 1198.
- [27] X. Zhang, H. Cheng, H. Zhang, Adv. Mater. 2017, 29.
- [28] J. N. Coleman, M. Lotya, A. O'Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, *Science* **2011**, 331, 568.
- [29] E. Singh, K. S. Kim, G. Y. Yeom, H. S. Nalwa, *ACS Appl. Mater. Inter.* **2017**, 9, 3223.
- [30] a) X. Huang, Z. Zeng, H. Zhang, *Chem. Soc. Rev.* 2013, 42, 1934. b) H. Zeng, G.-B. Liu, J. Dai, Y. Yan, B. Zhu, R. He, L. Xie, S. Xu, X. Chen, W. Yao, *Sci. Rep.* 2013, 3, 1608. c) S. Mouri, Y. Miyauchi, K. Matsuda, *Nano Lett.* 2013, 13, 5944.
- [31] V. Vohra, K. Kawashima, T. Kakara, T. Koganezawa, I. Osaka, K. Takimiya, H. Murata, *Nat. Photonics* **2015**, 9, 403.
- [32] D. K. Owens, Richmond, Virginia, R. C. Wendt, *Journal of Appied Polymer Science* **1969**, 13, 1741.
- [33] J.-K. Tan, R.-Q. Png, C. Zhao, P. K. H. Ho, Nat. Commun. 2018, 9, 3269.
- [34] W. Zhao, S. Li, H. Yao, S. Zhang, Y. Zhang, B. Yang, J. Hou, J. Am. Chem. Soc. 2017, 139, 7148.
- [35] Y. Qin, M. A. Uddin, Y. Chen, B. Jang, K. Zhao, Z. Zheng, R. Yu, T. J. Shin, H. Y. Woo, J. Hou, Adv. Mater. 2016, 28, 9416.
- [36] C. M. Proctor, M. Kuik, T.-Q. Nguyen, Prog. Polym. Sci. 2013, 38, 1941
- [37] N. Li, J. D. Perea, T. Kassar, M. Richter, T. Heumueller, G. J. Matt, Y. Hou, N. S. Guldal, H. Chen, S. Chen, S. Langner, M. Berlinghof, T. Unruh, C. J. Brabec, *Nat. Commun.* 2017, 8, 14541.
- [38] L. A. Perez, K. W. Chou, J. A. Love, T. S. van der Poll, D. M. Smilgies, T. Q. Nguyen, E. J. Kramer, A. Amassian, G. C. Bazan, *Adv. Mater.* **2013**, 25, 6380.
- [39] Y. Firdaus, L. P. Maffei, F. Cruciani, M. A. Müller, S. Liu, S. Lopatin, N. Wehbe, G. O. N. Ndjawa, A. Amassian, F. Laquai, P. M. Beaujuge, *Adv. Energy Mater.* 2017, 7, 1700834.
- [40] a) X. Gu, W. Cui, H. Li, Z. Wu, Z. Zeng, S.-T. Lee, H. Zhang, B. Sun, *Adv. Energy Mater.* 2013, 3, 1262. b) A. Kumar, H.-H. Liao, Y. Yang, *Org. Electron.* 2009, 10, 1615;
 c) M. Stephen, K. Genevičius, G. Juška, K. Arlauskas, R. C. Hiorns, *Polym. Int.* 2017, 66, 13.
- [41] X. Gu, W. Cui, H. Li, Z. Wu, Z. Zeng, S.-T. Lee, H. Zhang, B. Sun, Adv. Energy Mater. 2013, 3, 1262.

- [42] W. Xing, Y. Chen, X. Wang, L. Lv, X. Ouyang, Z. Ge, H. Huang, *ACS Appl. Mater. Inter.* **2016**, 8, 26916.
- [43] D. Konios, G. Kakavelakis, C. Petridis, K. Savva, E. Stratakis, E. Kymakis, J. Mater. Chem. A 2016, 4, 1612.
- [44] Z. Liu, J. Li, Z.-H. Sun, G. Tai, S.-P. Lau, F. Yan, *ACS Nano* **2012**, 6, 810.
- [45] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, 59, 1758.
- [46] G. F. Burkhard, E. T. Hoke, M. D. McGehee, *Adv. Mater.* **2010**, *22*, 3293.

Figures



Figure 1. a) Schematics illustrating the process of sonication-assisted liquid exfoliation used to prepare the MoS₂ and WS₂ suspensions. b) Absorption spectra of the as-prepared MoS₂ and WS₂ suspensions. Inset image demonstrates the Tyndall effect in both WS₂ and MoS₂ dispersions. c) Schematic illustration of the deposition of MoS₂ and WS₂ HTLs onto the substrate via spin-coating. d) Element mapping of In for ITO (blue), W for ITO/WS₂ (red), and Mo for ITO/MoS₂ (green) obtained using EDX (scale bar: $2 \mu m$). Insets show the corresponding AFM images of the surface topography of each sample ($1.3 \times 1.3 \mu m$).



Figure 2. Topography AFM images of PBDB-T-SF:IT-4F BHJ layers deposited onto a) ITO/PEDOT:PSS, b) ITO/WS₂, c) ITO/MoS₂, and d) ITO (scale bar: 1 μ m). e) Surface height histograms extracted from the AFM images in (a-d). f) The work function of ITO and various HTLs deposited on ITO measured via Kevin Probe (KP) technique and calculated via the DFT method.



Figure 3. a) Schematic of the standard cell architectures employed. b) Chemical structure of PBDB-T-SF and IT-4F used as the BHJ materials and their lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital energies.^[34] c) *J*-*V* curves, and d) quantum efficiency (QE) curves of PBDB-T-SF:IT-4F solar cells using WS₂, MoS₂, and PEDOT:PSS as the HTLs. Light intensity dependence of e) V_{OC} and f) J_{SC} , measured for the same cells. g) J_{SC}/J_{sat} vs. light intensity. h) Bimolecular recombination rate constant (k_{rec}) inferred from τ and *n*, as a function of *n*.



Figure 4. a) The chemical structure of PBDB-T-2F, Y6, and PC₇₁BM used in this study and the corresponding lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital energies.^[5] b) *J-V* curves of OPVs based on PBDB-T-2F:Y6 and PBDB-T-2F:Y6:PC₇₁BM with different HTLs. c) A comparison of the performance with previously reported OPVs with 2D material interfaces. QE curves of OPVs based on d) PBDB-T-2F:Y6, and e) PBDB-T-2F:Y6:PC₇₁BM active layer for different HTLs.

BHJ materials	HTL	J _{SC} [mA/cm ²]	<i>V</i> oc [V]	FF	PCE _{max} (PCE _{avg})[%]	R_{S} [Ω cm ²]
ד תחתת	WS_2	20.6 (20.0) ^a	0.88	0.74	13.5 (13.1±0.4) ^b	3.4
PDDD-1-	MoS_2	20.0 (19.3)	0.84	0.71	12.0 (11.8±0.2)	4.1
SF:IT-4F	PEDOT:PSS	20.2 (19.4)	0.90	0.72	13.1 (12.9±0.2)	3.7

Table 1. Summary of photovoltaic operating parameters for PBDB-T-SF:IT-4F OPVs made with different HTLs, measured under illumination of AM $1.5G (100 \text{ mW/cm}^2)$.

^a Data from EQE measurements.

^bAverage PCE values (PCE_{avg}) calculated from 15 cells.

Table 2. Summary of photovoltaic operating parameters for PBDB-T-2F:Y6 and PBDB-T-2F:Y6:PC₇₁BM OPVs made with different HTLs, measured under illumination of AM 1.5G (100 mW/cm^2).

BHJ materials	HTL	$J_{\rm SC}$ [mA/cm ²]	V _{OC} [V]	FF	PCE _{max} (PCE _{avg}) [%]	R_{S} [$\Omega \ cm^{2}$]
PBDB-T-2F:Y6	WS_2	25.9 (25.3) ^a	0.84	0.73	15.8 (15.3±0.5) ^b	3.0
	PEDOT:PSS	25.2 (24.8)	0.85	0.72	15.3 (14.9±0.4)	3.1
PBDB-T-2F:	WS_2	26.0 (25.5)	0.84	0.78	17.0 (16.5±0.5)	2.1
Y6: PC ₇₁ BM	PEDOT:PSS	25.5 (25.0)	0.85	0.75	16.4 (16.0±0.4)	2.5

^a Data from EQE measurement.

^bAverage PCE values (PCE_{avg}) calculated from 15 cells.

The use of liquid exfoliated two-dimensional WS₂ and MoS₂ as hole-transporting layers (HTLs) in ultra-high efficiency organic solar cells is reported. WS₂ yields cells with the higher power conversion efficiency (PCE), fill-factor, and short circuits current than MoS₂ and PEDOT:PSS. When WS₂ is introduced as HTL in PBDB-T-2F:Y6:PC₇₁BM organic solar cells, a maximum PCE value of 17% is achieved.

Keywords: 2D transition metal sulfides; hole transport layer; liquid exfoliation; nonfullerene organic solar cell; WS_2 and MoS_2 .

Yuanbao Lin, Begimai Adilbekova, Yuliar Firdaus, Emre Yengel, Hendrik Faber, Muhammad Sajjad, Xiaopeng Zheng, Emre Yarali, Akmaral Seitkhan, Osman M. Bakr, Abdulrahman El-Labban, Udo Schwingenschlögl, Vincent Tung, Iain McCulloch, Frédéric Laquai, Thomas D. Anthopoulos*

17% Efficient Organic Solar Cells Based on Liquid Exfoliated WS_2 as Replacement to PEDOT:PSS



Supporting Information

$17\,\%$ Efficient Organic Solar Cells Based on Liquid Exfoliated WS_2 as Replacement to PEDOT:PSS

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Figure S1. a) Low-resolution and b) high-resolution TEM images of the liquid exfoliated WS_2 . c) Low-resolution and d) high-resolution TEM images of the liquid exfoliated MoS_2 . The insets in b) and d) are the corresponding Fast Fourier Transform (FFT) patterns of the lattice. Raman spectra of e) WS_2 and f) MoS_2 flakes spin-coated on Si substrates where the presence of 1L, 2L and 3L is clearly evidenced.



Figure S2. AFM images of: a) ITO, b) ITO/WS₂, and c) ITO/MoS₂. d) Height histograms extracted from the AFM images. The shift in the height histogram peak for the pristine ITO observed upon spin-coating of the WS₂ and MoS₂, is indicative of flattening/smoothening of its surface. AFM images of WS₂ e), and MoS₂ f) spun on SiO₂. g) Height histograms of the AFM images. WS₂ flakes appears to be larger in size and thinner than MoS₂.

S1. Owen Method for calculating the surface energy

The Owen's method is often used to calculate the surface energy:

$$\gamma_S = \gamma_S^D + \gamma_S^P, \gamma_l = \gamma_l^D + \gamma_l^P \tag{SI-1}$$

where γ_s is is composed of the dispersion force γ_s^D and polarity force γ_s^P . Similarly, γ_l is the surface energy of the liquid and consists of a dispersion force γ_l^D and polarity force γ_l^P . Then:

$$\gamma_l (1 + \cos\theta) = 2(\gamma_s^D \gamma_l^D)^{1/2} + 2(\gamma_s^P \gamma_l^P)^{1/2}$$
(SI-2)

If the surface energies γ_l^D and γ_l^P of the testing liquid are known and its contact angle on solid surface is measured, there are still two unknown quantities (γ_s^D, γ_s^P) remaining in the above formula. To determine γ_s^D and γ_s^P two known testing liquids are required.

$$\gamma_{l1}(1 + \cos\theta_1) = 2(\gamma_s^D \gamma_{l1}^D)^{1/2} + 2(\gamma_s^P \gamma_{l1}^P)^{1/2}$$
(SI-3)

$$\gamma_{l2}(1 + \cos\theta_2) = 2(\gamma_s^D \gamma_{l2}^D)^{1/2} + 2(\gamma_s^P \gamma_{l2}^P)^{1/2}$$
(SI-4)

Once the γ_s^D and γ_s^P are obtained, γ_s can be determined using $\gamma_s = \gamma_s^D + \gamma_s^P$.



Figure S3. Photographs of water (top row) and formamide (bottom row) droplets in contact with the various surfaces. ^aITO is spin-coated with ethanol:water (1:1) and dried at room temperature before contact angle measurement.

	Table S1.	Parameters	of the	testing	liquids	used in	n the surface	energy	measurements.
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Liquid	Polar force $[\gamma_l^P]$	Dispersion force $[\gamma_l^D]$	Surface energy $[\gamma_l]$	γ_l^P/γ_l^D
Water	51	21.8	72.8	2.36
Formamide	18.7	39.5	58.2	0.47

Table S2	. Summary of	f the measu	ed contac	t angles	, surfac	e energie	es and	work	functi	ion f	or th	1e
various su	urfaces and sa	amples.										

Surface	Water contact angle ^a	Formamide contact angle	Surface energy [mN/m] ^b
ITO	41°	16°	58.8
WS ₂	12°	12°	71.5
MoS ₂	16°	20°	70.7
PEDOT:PSS	40°	45°	58.3
ITO ^c	11°	29°	74.0

^aValues represent average contact angles measured from 5 samples.

^bSurface energy was calculated using the Owen method described in Section S1.

^cITO spin-coated with ethanol:water (1:1) and dried at room temperature.



Figure S4. Average electrostatic potential calculated for the various materials/systems studied. In all plots, E_V is the vacuum energy and E_F is the Fermi energy. a) Monolayer WS₂, b) bilayer WS₂, and c) trilayer WS₂. d) Monolayer MoS₂, e) bilayer MoS₂, and f) trilayer MoS₂.

Table S3. Work function values experimentally measured and theoretically calculated for ITO, WS₂, MoS₂ and PEDOT:PSS.

Solid surface	Work function [eV] ^a	Work function [eV] ^b
ITO	-4.7	-4.7
ITO/WS ₂	-5.5	-5.7 (1L) / -5.3 (2L) / -5.2 (3L)
ITO/MoS ₂	-5.4	-5.9 (1L) / -5.6 (2L) / -5.4 (3L)
ITO/PEDOT:PSS	-4.8	n.a.

^aWork functions were measured using the Kelvin Probe (KP) technique. ^bWork functions calculated using DFT, where 1L, 2L, and 3L refer to monolayer, bilayer and trilayer WS₂ and MoS₂, respectively.



Figure S5. a) *J-V* curves of OPV cells based on PBDB-T-SF:IT-4F where the HTL was spincoated at different spin speeds. b) *J-V* curves of OPV cells based on PBDB-T-SF:IT-4F for which the MX_2 suspensions were prepared at different centrifuging speeds and spin-coated onto ITO electrodes at 1500 rpm.

Table S4. Photovoltaic parameters of PBDB-T-SF:IT-4F solar cells incorporating HTLs of WS_2 and MoS_2 that have been prepared at different spin-coating speeds. All cells were tested under standard illumination of AM 1.5G (100 mW/cm²).

HTL	Spin-coating speed (rpm)	$J_{\rm SC}$ [mA/cm ²]	V _{OC} [V]	FF	PCE _{max} [%]
	800	18.5	0.89	0.72	11.8
WS_2	1500	19.5	0.88	0.73	12.6
	3000	18.3	0.87	0.73	11.7
	800	19.3	0.84	0.66	10.6
MoS ₂	1500	19.1	0.84	0.71	11.4
	3000	18.0	0.80	0.65	9.5
w/o	-	15.3	0.61	0.63	5.8

Table S5. Photovoltaic parameters of PBDB-T-SF:IT-4F solar cells incorporating HTLs of WS_2 and MoS_2 that have been prepared at different centrifuge speeds and spin-coated onto ITO at 1500 rpm. All cells were tested under standard illumination of AM 1.5G (100 mW/cm²).

HTL (MX ₂)	Centrifuge speed (rpm)	$J_{\rm SC}$ [mA/cm ²]	V _{OC} [V]	FF	PCE _{max} [%]
WS ₂	4000	18.3	0.87	0.73	11.6
	6000	19.5	0.88	0.73	12.6
	8000	19.1	0.88	0.72	12.0
MoS ₂	6000	18.6	0.83	0.68	10.5
	8000	19.1	0.84	0.71	11.4
	10000	18.8	0.84	0.71	11.1



Figure S6. EQE, IQE, reflectance, and parasitic absorption spectra of OPV cells based on PBDB-T-SF:IT-4F incorporating a) WS₂, b) MoS₂, and c) PEDOT:PSS HTLs. d) Absorption spectra of the various HTL systems deposited onto ITO. For the ITO/WS₂ and ITO/MoS₂ samples, a shift in the apparent absorption feature of ITO centered at \approx 455 nm towards longer wavelengths (\approx 480 nm), is observed and is attributed to the presence of the few-layer TMDs atop the ITO. The latter shift is most likely the result of a change in the photonic structure of the sample occurring upon deposition of the TMDs on ITO. Evidence of this difference can be seen in the reflection spectra of cells based on a) WS₂ and b) MoS₂, and that of c) PEDOT:PSS cell.



Figure S7. Optical simulations for the electric field intensity $|\mathbf{E}|^2$ and exciton generation rate profiles in the studied BHJ OPV devices for three different wavelengths (400 nm, 600 nm, and 700 nm).



Figure S8. *J*-*V* curves *vs.* light intensity for OPV cells incorporating: a) WS₂, b) MoS₂, and c) PEDOT:PSS as the HTL. d) Charge carrier lifetime (τ) and e) carrier density *vs.* light intensity, and f) carrier density *vs.* τ .



Figure S9. Dark *J-V* curves of OPV cells based on PBDB-T-SF:IT-4F with different HTLs.



Figure S10. a-c) Photo-CELIV transients recorded for the various OPV cells based on PBDB-T-SF:IT-4F at constant voltage and ramp rate. d) Dependence of mobility as a function of light intensity.



Figure S11. *J-V* curves of OPV cells with PEDOT:PSS based on PBDB-T-2F:Y6:PC₇₁BM photoactive layers of different compositions (wt%).

PBDB-T-2F:Y6:PC71BM	$J_{\rm SC}$ [mA/cm ²]	V _{OC} [V]	FF	PCE _{max} (PCE _{avg}) [%]
1:1.2:0	25.2	0.85	0.72	15.3 (14.9±0.4)
1:1:0.2	25.5	0.85	0.75	16.4 (16.0±0.4)
1:0.7:0.5	24.5	0.87	0.68	14.5 (13.9±0.6)
1:0.3:0.7	18.0	0.88	0.58	9.2 (8.7±0.5)
1:0:1.2	12.9	0.97	0.57	7.2 (6.9±0.3)

Table S6. Photovoltaic parameters of OPVs based on PBDB-T-2F:Y6:PC₇₁BM with different compositions and PEDOT:PSS as the HTL. All cells were tested under standard illumination of AM 1.5G (100 mW/cm²).



Figure S12. EQE, IQE, reflectance, and parasitic absorption spectra of OPV cells based on binary PBDB-T-2F:Y6 and ternary PBDB-T-2F:Y6:PC₇₁BM BHJ OPV with different HTLs. Binary PBDB-T-2F:Y6 BHJ with a) WS₂ and b) PEDOT:PSS as the HTLs. Ternary PBDB-T-2F:Y6:PC₇₁BM BHJ with c) WS₂ and d) PEDOT:PSS as the HTLs.