Unveiling Charge-Transport Mechanisms in Electronic Devices Based on Defect-Engineered MoS$_2$ Covalent Networks

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Device performance of solution-processed 2D semiconductors in printed electronics has been limited so far by structural defects and high interflake junction resistance. Covalently interconnected networks of transition metal dichalcogenides potentially represent an efficient strategy to overcome both limitations simultaneously. Yet, the charge-transport properties in such systems have not been systematically researched. Here, the charge-transport mechanisms of printed devices based on covalent MoS$_2$ networks are unveiled via multiscale analysis, comparing the effects of aromatic versus aliphatic dithiolated linkers. Temperature-dependent electrical measurements reveal hopping as the dominant transport mechanism: aliphatic systems lead to 3D variable range hopping, unlike the nearest neighbor hopping observed for aromatic linkers. The novel analysis based on percolation theory attributes the superior performance of devices functionalized with π-conjugated molecules to the improved interflake electronic connectivity and formation of additional percolation paths, as further corroborated by density functional calculations. Valuable guidelines for harnessing the charge-transport properties in MoS$_2$ devices based on covalent networks are provided.

1. Introduction

The discovery and isolation of 2D materials (2DMs) represent veritable breakthroughs in materials science owing to their wide-ranging portfolio of electronic and optoelectronic properties,[1] paving the way for disruptive and exotic technologies such as More-than-Moore and Internet-of-Things devices.[2] In the past two decades, tremendous research efforts have been devoted to developing novel methods and strategies for the large-scale production of 2DMs, aiming for the best trade-off among quality, high throughput, and low cost.[3] Solution processing represents the most effective protocol to attain high-concentration and high-volume dispersions (also referred to as "inks") of 2DMs; among them, liquid phase exfoliation is an efficient strategy to convert bulk layered materials into thin nanosheets dispersed in a suitable solvent.[4] These inks can be printed into thin films using several approaches, including inkjet printing, screen printing, and spray coating,[5] thereby promoting the advances of 2DM-printed electronics where low-cost and large-area fabrication is as relevant as device performance. In this regard, the ever-growing interest in 2D semiconductors for (opto)electronics has led to the great success of transition metal dichalcogenides (TMDs). Their extremely versatile physicochemical properties ensure a broad range of applicability, further expanded through ad hoc functionalization strategies using molecular chemistry approaches.[6–11] Nevertheless, progress is still hampered by structural defects, negatively

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impacting their electronic properties and, thereby, device performance.[12] Furthermore, the poor interflake electronic connectivity (viz. high interflake electrical resistance) significantly impedes the charge carrier transport, constituting a major bottleneck in the development of TMD-printed (opto)electronics, especially in large-area and high-performance device applications.[13] Recently, we have devised an innovative molecular functionalization strategy to simultaneously overcome both limitations, by healing the most abundant structural defects in solution-processed TMDs (i.e., sulfur vacancies, V_S) and bridging adjacent flakes by using π-conjugated dithiolated molecules, thereby leading to the formation of covalently interconnected networks with enhanced electrical performance.[14] Although the charge-transport mechanisms in individual TMD nanosheets have already been meticulously studied,[15–17] very few similar studies have been performed on thin films.[18] More importantly, little is known about transport in TMD covalent networks, leaving a significant and crucial gap in our understanding. In this article, we unveil the charge-transport mechanisms in solution-processed covalent MoS$_2$ networks by investigating their temperature-dependent electrical conductivity. The MoS$_2$ ink, prepared by ultrasonication, is first deposited into ≈500 nm thick films via spray coating on bare or electrode-patterned Si/SiO$_2$ substrates. Then, the MoS$_2$ functionalization is performed under nitrogen-controlled atmosphere using a 50 mM solution of i) π-conjugated 1,4-benzenedithiol (BDT) or ii) aliphatic 1,3-propanedithiol (PDT)

in anhydrous hexane, yielding the related covalent networks (Experimental Section). The in-depth multiscale investigation of covalent MoS$_2$ networks is reported elsewhere.[14] In a joint experimental and theoretical investigation, we prove that the charge transport in MoS$_2$ films and networks is dominated by interflake hopping, whose efficiency and detailed mechanism critically depend on the chemical structure of the linker.

2. Results and Discussion

2.1. Terahertz Spectral Analysis: MoS$_2$ Films and Networks

To shed light on the electrical transport properties of MoS$_2$ films and covalent networks, we exploit optical-pump terahertz (THz)-probe spectroscopy. Due to the transient nature of THz pulses, charge carriers are locally driven over a short distance (approximately tens of nanometers), mainly probing the intraflake transport properties[19–21] and complementing the measurements performed on electrical devices, where both intra- and interflake contributions occur. As displayed in the schematic of **Figure 1**a, optical excitation (i.e., laser pulses with a duration of ≈50 fs and photon energy of 3.10 eV) injects charge carriers in MoS$_2$ samples, whose photoconductivity ($\Delta\sigma_{ph}$) is sequentially probed by a single cycle THz pulse (with a peak electric field equal to E). The $\Delta\sigma_{ph}$ can be extrapolated from the photoinduced THz absorption following $\Delta\sigma_{ph} \propto -\Delta E/E$ (with
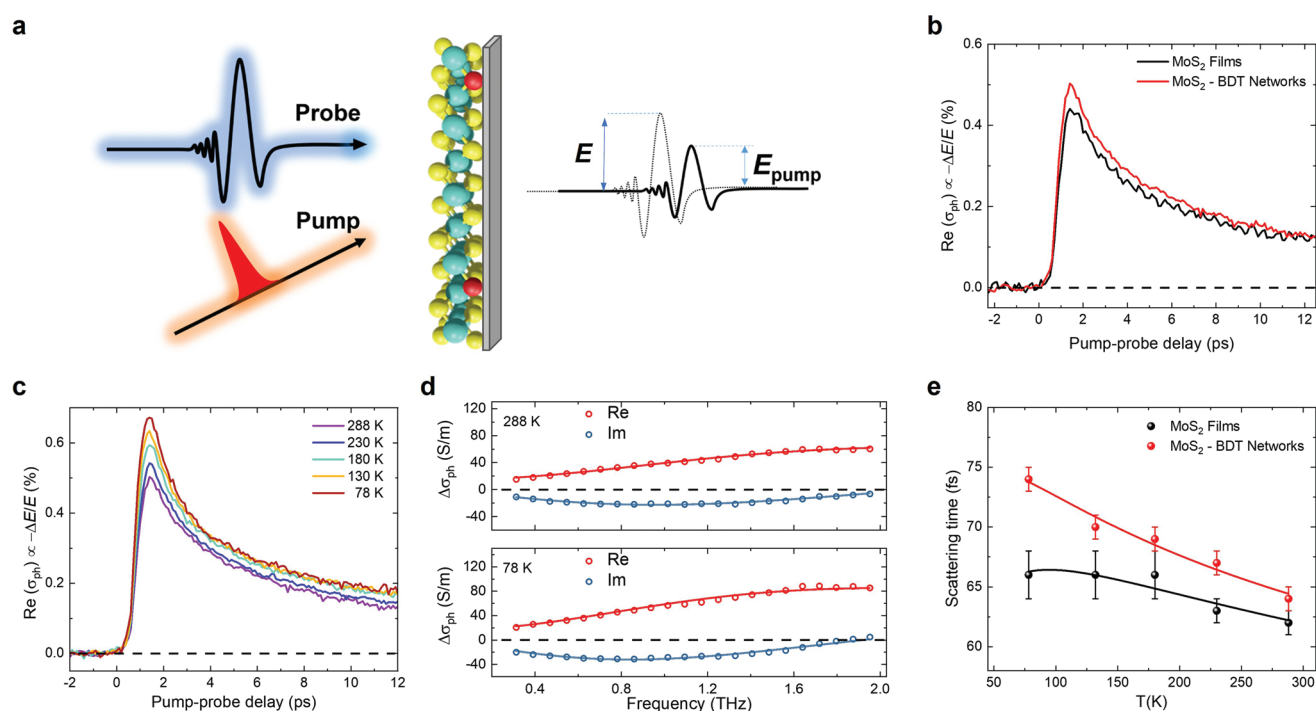

Figure 1. THz spectral analysis on MoS$_2$ films and covalent networks. a) Schematic illustration of optical-pump–THz-probe spectroscopy on MoS$_2$ systems. b) Photoconductivity dynamics of pristine MoS$_2$ films and MoS$_2$–BDT networks (absorbed photon density ≈10^{17} m^{-2}). c) Photoconductivity dynamics of MoS$_2$–BDT networks within the T range 288–78 K under vacuum conditions (≈10^{-4} mbar). d) Complex photoconductivity spectra for MoS$_2$–BDT networks at 288 and 78 K, recorded ≈2 ps after photoexcitation (red circles: real photoconductivity; blue circles: imaginary photoconductivity). The solid lines represent the data fitting using the Drude–Smith model. e) Scattering time as a function of T for pristine MoS$_2$ films and MoS$_2$–BDT networks. The solid lines in (e) show a simple model (Experimental Section) for electron–phonon coupling (identical for both systems) and impurity scattering (enhanced for MoS$_2$ films).

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$\Delta E = E_{pump} - E$, where E_{pump} represents the transmitted THz field from the sample with photoexcitation).[19] We find that $\Delta\sigma_{ph}$ of MoS$_2$–BDT networks increases by ≈10% compared to pristine MoS$_2$ films (Figure 1b), and a similar enhancement factor of $\Delta\sigma_{ph}$ is recorded for MoS$_2$–PDT networks as well (Section S2, Supporting Information). Such observations support the passivation of V$_S$ by BDT and PDT molecules (viz., decreasing the overall defect density) and thus the resulting increase of $\Delta\sigma_{ph}$, regardless of the chemical structure of the linkers, i.e., aromatic versus aliphatic. To further investigate the intraflake charge-transport properties in MoS$_2$ films and networks, as well as to disentangle its contribution from the overall conductivity in electrical devices, we conduct temperature (T)-dependent $\Delta\sigma_{ph}$ measurements.

Figure 1c shows that $\Delta\sigma_{ph}$ of MoS$_2$–BDT networks increases upon lowering the temperature from 288 to 78 K. Such a behavior is typical for band-like transport, with charge carrier mobility within MoS$_2$ flakes limited by the carrier–phonon scattering.

The Drude–Smith model (Experimental Section), widely used to explain charge transport in nanomaterials,[19,22,23] well describes and fits our experimental data (Figure 1d). The inferred T-dependent charge scattering times for pristine MoS$_2$ films and MoS$_2$–BDT networks are displayed in Figure 1e.

The charge scattering time in both MoS$_2$ films and MoS$_2$–BDT networks increases with decreasing T, in agreement with phonon-scattering-limited band-like transport within MoS$_2$ flakes. Moreover, we analyze the T-dependent scattering time assuming contributions from phonon and impurity scatterings (Experimental Section). This data analysis reveals an ≈40% decrease in the carrier–defect scattering rate for MoS$_2$–BDT networks compared with pristine MoS$_2$ films, demonstrating the positive effect of the thiol group on the healing of V$_S$.

MoS$_2$ electrical devices show a thermally activated charge carrier transport and an increase of the device figures of merit by one order of magnitude upon BDT functionalization.[14]

Thus, the modest transport enhancement recorded for the intraflake contribution via THz analysis (≈10% at room temperature) provides unambiguous evidence that the performance in MoS$_2$ electrical devices is dominated by interflake transport, whose mechanisms are discussed below.

2.2. Charge Carrier Transport: Hopping Mechanisms in MoS$_2$ Devices

Charge carrier transport in polycrystalline, highly disordered, and defective materials is generally governed by hopping between localized defective states.[24–27] To shed light on the charge-transport mechanisms involved in MoS$_2$ films and networks (**Figure 2**a), we investigate their T-dependent electrical conductivity (σ). To this end, we carry out two-point probe measurements and assess the electrical device performance from 340 to 5 K (Figure 2b). The maximum σ for MoS$_2$–PDT networks is higher than pristine films by a factor 3 ± 1, confirming our previously reported data and highlighting the effects of thiolated systems on the healing of V$_S$ in TMDs.[14] Conversely, the network formation with aromatic BDT molecules increases σ by one order of magnitude.

As shown in the inset of Figure 2b, two different regimes can be recognized in the σ versus T plots: i) a thermally activated regime (hopping regime), in the T range 340–200 K, with an exponential dependence of σ on T; ii) a T-independent behavior (tunneling regime) between 150 and 5 K.[28] In the transition region (200–150 K), tunneling and hopping regimes occur simultaneously.[29]

In the tunneling regime, the functionalization of pristine MoS$_2$ films with dithiolated molecules does not affect the $\sigma(T)$ curves, unlike significant variations observed in the hopping region. We identify the hopping mechanisms by extracting the exponent α from the data, with $\alpha \le 1$, using the equation

$$\sigma(T) = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^\alpha\right] = \frac{1}{\rho(T)} \tag{1}$$

with σ_0, T_0, and ρ representing the prefactor, characteristic temperature, and resistivity of the system, respectively. For $\alpha = 1$, $\sigma(T)$ is proportional to $\exp(E_a/k_B T)$, where $E_a = k_B T_0$ defines the activation energy of the nearest neighbor hopping (NNH) mechanism,[24,25] which involves the hop of the charge carrier between the two spatially nearest trap sites, despite their energy levels. On the contrary, all variable range hopping (VRH) mechanisms display $\alpha < 1$, and the transport is ruled by charge carrier hopping between the two most energetically favorable sites, regardless of their spatial distance.[30,31]

In particular, the Mott-VRH mechanisms exhibit $\alpha = 1/(1+d)$, where d is the dimensionality of the system (e.g., $\alpha = 1/4$ for 3D Mott VRH). A different mechanism known as Efros–Shklovskii VRH (ES-VRH) arises for $\alpha = 1/2$, where a Coulomb gap is opened in the density of states (DOS) at the Fermi level, and the hopping transport is strongly affected by Coulomb scattering of the charge carriers with charged centers.[32,33] Thus, we extract α to reveal the interflake hopping mechanisms involved in each of our systems. We first calculate the reduced activation energy (W)

$$W = -\frac{T}{\rho}\frac{d\rho}{dT} \tag{2}$$

Upon linearization of Equation (2), the slope of $\ln(W)$ versus $\ln(T)$ plot returns α. The three systems under investigation show distinct hopping mechanisms (Figure 2c). Pristine MoS$_2$ films exhibit $\alpha = 1/2$, indicating an ES-VRH mechanism governed by the scattering of the charge carriers with fixed charged centers. For MoS$_2$–PDT networks and MoS$_2$–BDT networks, we extract $\alpha = 1/4$ and $\alpha = 1$, respectively. The aliphatic PDT molecules, upon healing of V$_S$, neutralize the Coulombic scattering centers involved in the hopping mechanism of pristine MoS$_2$ films and, thus, lead to a transition from ES-VRH to 3D Mott VRH.[15,16,18,34,35] A transition to the hopping mechanism is also recorded for the functionalization with π-conjugated BDT molecules, where we observe a change from ES-VRH, characteristic of pristine MoS$_2$ films, to NNH mechanism. The aromatic ring enhances the interflake transport by bridging two adjacent flakes and improving their electronic connectivity, thereby creating favorable conduction paths for the charge carriers, as supported by the theoretical calculations reported below.

Furthermore, we extrapolate the average hopping distance (R_{hop}) for the three systems by using the characteristic
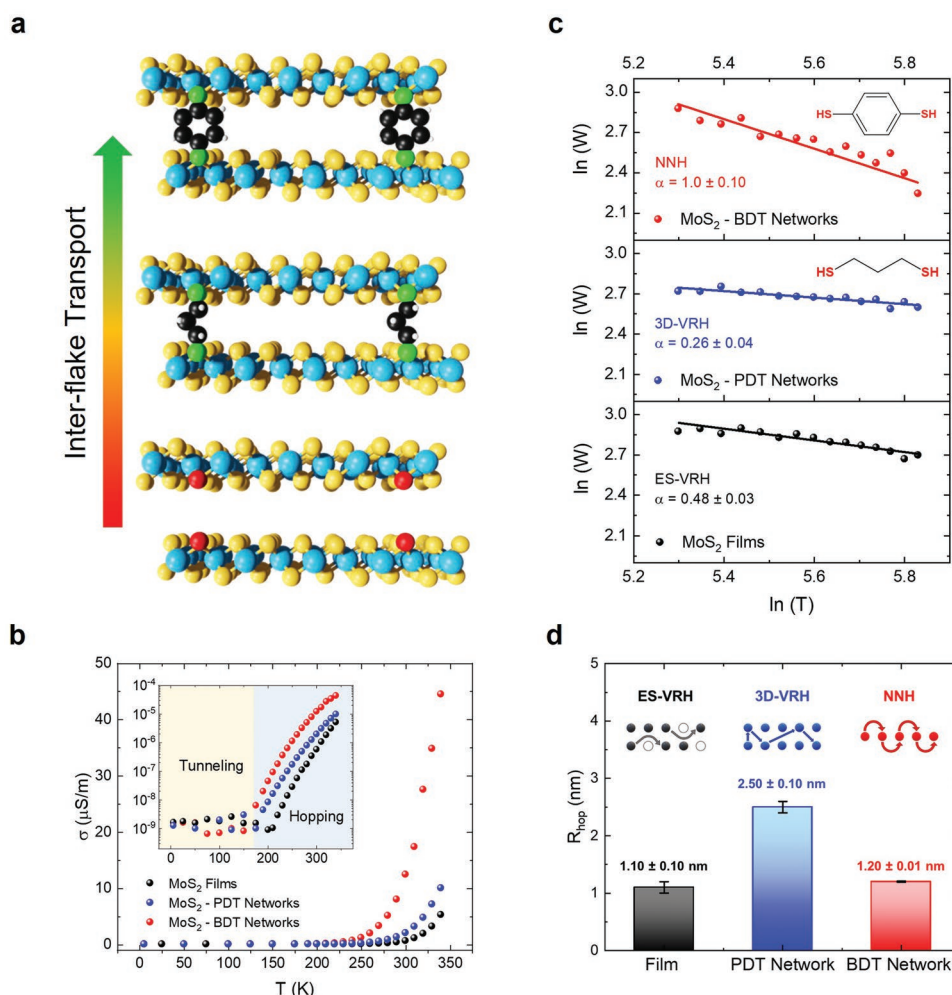
Figure 2. Charge-transport analysis in printed MoS_2 devices. a) Sketch of V_S healing mechanism and network formation in pristine MoS_2 films by aliphatic PDT and aromatic BDT molecules, highlighting the effects on the interflake charge transport. Atom color legend: sulfur (yellow), molybdenum (light blue), sulfur vacancy (red), sulfur healing (green), carbon (black), hydrogen (light gray). b) σ versus T plots for MoS_2 films, MoS_2–PDT networks, and MoS_2–BDT networks. Inset: σ versus T curves displayed on a logarithmic scale. All curves are recorded with $V = 10$ V. c) $\ln(W)$ versus $\ln(T)$ plots for MoS_2 films, MoS_2–PDT networks, and MoS_2–BDT networks. All α values are extracted at $V = 1$ V. d) Extrapolated R_{hop} for MoS_2 films, MoS_2–PDT networks, and MoS_2–BDT networks, along with a sketch of their hopping mechanisms.

equations related to each hopping mechanism (Experimental Section). A sketch of the hopping mechanisms as well as the extrapolated R_{hop} for the systems under investigation are displayed in Figure 2d. The increase in R_{hop} moving from pristine MoS_2 films ($R_{ES\text{-}VRH} = 1.10 \pm 0.10$ nm) to MoS_2–PDT networks ($R_{3D\text{-}VRH} = 2.50 \pm 0.10$ nm) is ascribed to the healing of V_S and, thus, the decrease of the overall defect density. The R_{hop} for MoS_2–BDT networks $R_{NNH} = 1.20 \pm 0.01$ nm points to different and additional effects upon healing of V_S and network formation. In fact, MoS_2 networks produced with π-conjugated BDT linkers benefit from an exclusive enhanced interflake electronic connectivity (i.e., reduced interflake resistance), promoting enhanced hopping transport through adjacent flakes. Comparing the R_{hop} for MoS_2–PDT ($R_{3D\text{-}VRH} = 2.50 \pm 0.10$ nm) and MoS_2–BDT networks ($R_{NNH} = 1.20 \pm 0.01$ nm), the latter value suggests that the hop of a charge carrier occurs from a hopping site to the spatially closest one through the BDT bridging molecule, whose length is ≈0.7 nm.

2.3. Density Functional Theory (DFT) Calculations of Covalent MoS_2 Networks

To understand the role of dithiolated molecules during the healing of V_S and network formation, as well as related effects on the interflake charge transport, DFT calculations are performed on bulk pristine MoS_2 crystals, bulk defective MoS_2 crystals (with V_S), MoS_2–BDT, and MoS_2–PDT networks. The MoS_2 crystal structure we consider for this study contains one layer per unit cell, where the interflake stacking (along the c-axis) replicates the AA stacking mode.[36]

Starting from the pristine MoS_2 crystals with one layer per unit cell (**Figure 3**a), V_S are created by removing two sulfur atoms (referred to as MoS_2–$2V_S$) either directly on top of each other or diagonally to each other (Section S4, Supporting Information), such that the V_S concentration is kept at 6% in both cases, consistent with previous reports.[37,38] Of such two configurations, the latter is found to be energetically more
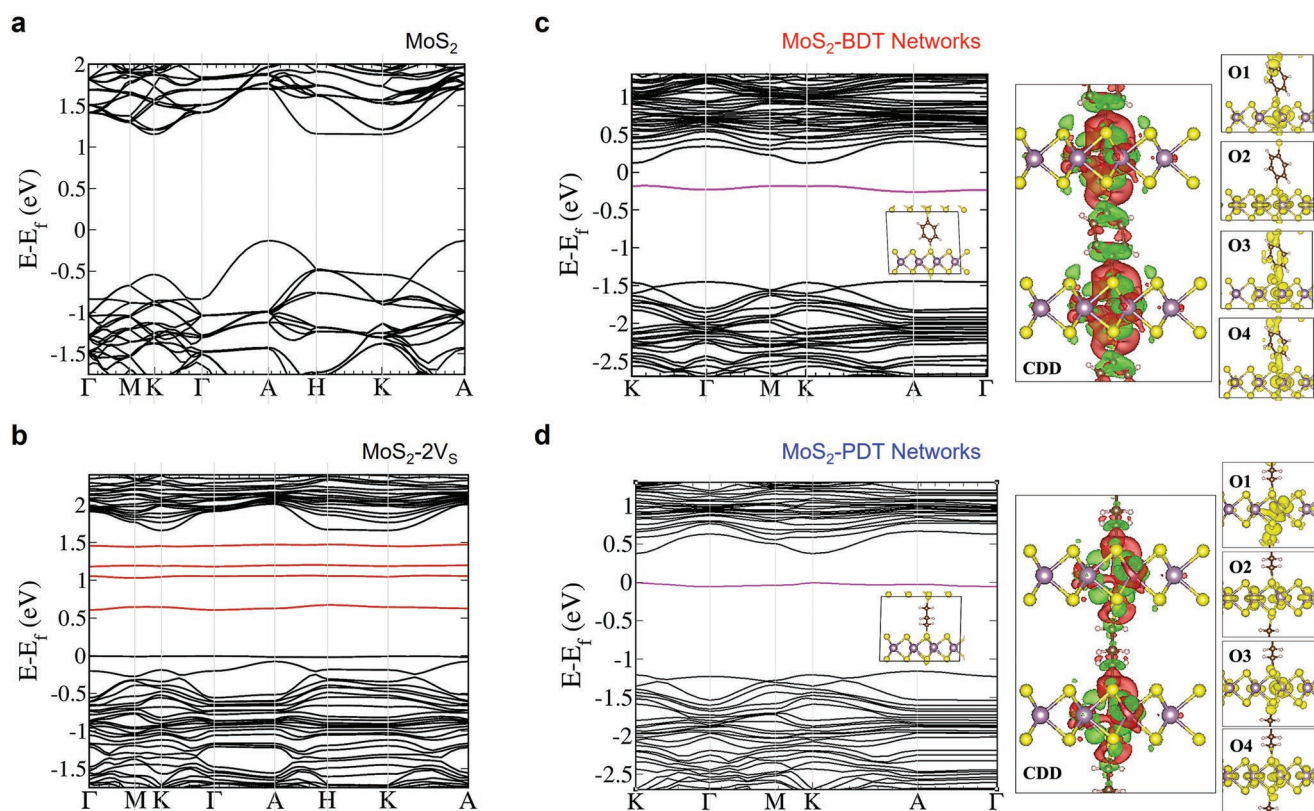
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Figure 3. DFT calculations for MoS$_2$ films and covalent networks. a,b) Electronic band structure of bulk MoS$_2$ crystal in its pristine (a) and defective (b) form (MoS$_2$–2V$_S$, with 6% V$_S$). c,d) Electronic band structure of MoS$_2$–BDT (c) and MoS$_2$–PDT (d) covalent networks (left panel). CDD plots (central panel) and crystalline orbitals (right panel) are also displayed. O1, O2, and O4 represent the crystalline orbitals (obtained at the K-point) of the occupied mid-gap state, the lowest unoccupied electronic state (LUCO, i.e., CBE), and the electronic state immediately following the CBE (LUCO + 1), respectively. O3 represents the LUCO in the middle of K–A path.

favorable by ≈20 meV per fractional unit when compared to the former, presenting defect states spread through the electronic bandgap (Figure 3b) which act as scattering centers and, thus, diminish the electron mobility.[39,40] When the structural defects are exposed to BDT and PDT molecules, the localized empty mid-gap defect states disappear, thereby restoring the electronic structure of pristine MoS$_2$ crystals. We also note that occupied mid-gap states appear within the electronic bandgap, as indicated by the magenta curves in Figure 3c,d.

When a BDT molecule is used to connect two MoS$_2$–2V$_S$ surfaces (Figure 3c, left panel), these mid-gap states are delocalized both on the BDT molecule and the underlying MoS$_2$–2V$_S$ surfaces, indicating a strong hybridization for such a dyad. The charge density difference (CDD) plots (Figure 3c, central panel) also display a strong delocalization of the electron density through the bridging BDT molecule connecting the two MoS$_2$–2V$_S$ flakes. Most importantly, such a strong hybridization between BDT molecules and MoS$_2$–2V$_S$ surfaces is also observed in the crystalline orbitals around the conduction band edge (CBE) (Figure 3c, right panel). On the contrary, in the case of PDT molecules (Figure 3d, left panel), the electron density from the two MoS$_2$–2V$_S$ surfaces through the aliphatic molecule hardly extends (Figure 3d, central panel), and the crystalline orbitals around the CBE do not show any significant contribution from the PDT molecule (Figure 3d, right panel).

The electronic structure of MoS$_2$–BDT networks as well as their CDD and orbital plots provide an unambiguous indication that π-conjugated BDT molecules not only heal the localized mid-gap defect states due to V$_S$ but also bridge two adjacent MoS$_2$–2V$_S$ flakes, improving their interflake electronic connectivity. Conversely, aliphatic PDT molecules do not provide a similar enhancement, as they solely induce the healing of localized mid-gap defect states and the recovery of the electronic structure of pristine MoS$_2$ crystals.

Moreover, we calculate the electron effective mass (m^*) at the CBE for the three systems under investigation. Remarkably, the m^* in MoS$_2$–BDT networks is significantly lower than MoS$_2$–2V$_S$ and MoS$_2$–PDT networks, being comparable to that of pristine MoS$_2$ crystals and highlighting an enhanced interflake electronic connectivity and charge transport (Table S4, Supporting Information).

2.4. Covalent MoS$_2$ Networks for Flexible Electronic Applications

For our electrical characterization, thin-film transistors (TFTs) are produced by spray coating MoS$_2$ films onto prepatterned substrates with interdigitated gold electrodes (Au-IDEs, serving as source and drain electrodes) and coplanar gate configuration. All steps related to the device fabrication, deposition,
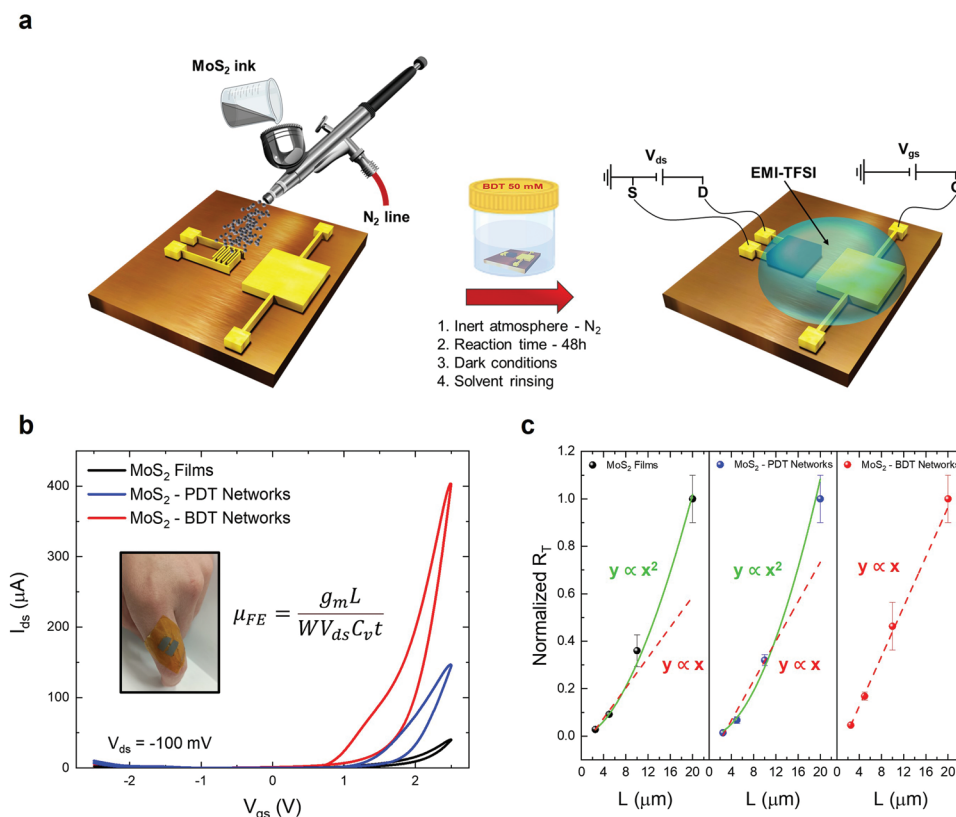
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Figure 4. Electrical characterization of printed MoS_2 devices. a) Cartoon of MoS_2 deposition, functionalization, and electrical characterization. b) Transfer characteristics for MoS_2 films, MoS_2–PDT networks, and MoS_2–BDT networks, recorded using EMI–TFSI as electrolyte gate. Inset: printed TFT device on PI flexible substrate. c) Normalized R_T versus L plots for MoS_2 films, MoS_2–PDT networks, and MoS_2–BDT networks, based on their TLM analysis performed in two-point probe configuration. R_T is calculated at 10 V for all systems. In the experimental data, the allometric and linear fits are displayed for MoS_2 films (left), MoS_2–PDT networks (middlel), and MoS_2–BDT networks (right).

and functionalization procedures are proved to be compatible with both rigid (Si/SiO$_2$) and flexible polyimide (PI) substrates (Kapton tape), supporting the progress of printed devices in flexible electronics (**Figure 4**a).

It is known that dielectric-gated TFTs based on solution-processed TMDs exhibit poor current switching ($I_{ON}/I_{OFF} < 10$),[41] encouraging the use of an electrolyte solution that modulates the device volumetrically.[14,42,43] In our devices, MoS_2 films and networks are gated by 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMI–TFSI) ionic liquid (IL), where the application of a gate voltage (V_{gs}) induces the formation of an electrical double layer at the IL/MoS_2 interface and results in a strong current modulation.[14,42,43] The typical transfer curves for pristine MoS_2 films, MoS_2–BDT networks, and MoS_2–PDT networks, recorded on PI substrates, are displayed in Figure 4b. As previously reported,[14] the electrical characteristics of TFTs based on MoS_2–BDT networks outperform those of pristine MoS_2 films and MoS_2–PDT networks, exhibiting an increase by one order of magnitude in the main device figures of merit. In particular, MoS_2–BDT networks reach field-effect mobilities and I_{ON}/I_{OFF} ratios up to 10^{-2} cm^2 V^{-1} s^{-1} and to 10^4, respectively (Table S5, Supporting Information), as a result of the improved interflake electronic connectivity.

For both MoS_2 film and network devices (in dry state, i.e., absence of IL), we take advantage of the transfer length method

(TLM) to extrapolate the contact resistance (Section S5, Supporting Information) and assess its influence on the total device resistance (R_T). To this end, we fabricate Au-IDEs with four different channel lengths (L) and investigate the R_T versus L behavior for the three systems under analysis, deriving R_T from their characteristic I–V curves. From TLM on pristine MoS_2 films (Figure 4c, left panel), our experimental data do not comply with the theoretical linear behavior of the R_T versus L (red curve), showing a quadratic dependence on L (green curve) instead, thereby highlighting a $1/L$ trend for σ. An identical behavior is observed upon using aliphatic linkers, with MoS_2–PDT networks showing a similar trend to pristine MoS_2 films (Figure 4c, central panel). Notably, MoS_2–BDT networks exhibit the ideal linear dependence of R_T on L (Figure 4c, right panel), owing to the improved interflake electronic connectivity upon dithiol functionalization.

Printed devices based on solution-processed TMDs represent highly porous aggregates of 2D rigid nanosheets, where morphological imaging by electron microscopy reveals a limited area of physical overlap among adjacent flakes, thereby yielding a high junction resistance and hindering the overall charge carrier transport.[13] The morphology, structural disorder, and defective nature of our multiflake systems are responsible for the dominant interflake resistance, where the physical and electronic connectivity among nanosheets defines a percolative pattern in-between the electrodes.

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2.5. Percolation Theory: Random Resistor Networks

The abovementioned anomalous dependence of σ on L is due to the percolation process occurring within the channels of our electrical devices, and it can be discussed and rationalized within the framework of random resistor networks.[44,45] The channel can be modeled as a 2D random resistor network, where the probability to find a bond (i.e., resistor of the percolation path) is given by p (**Figure 5**a).

Here, the effective conductivity (σ_{eff}) at criticality (i.e., percolation threshold $p = p_c$) scales as

$$\sigma_{\text{eff}}(L) \sim L^{-\beta} \qquad (3)$$

with $\beta = 0.95 \pm 0.01$.[44] Slightly above criticality, σ_{eff} is expected to follow the critical behavior for short enough L, reaching then a constant value proportional to $(p - p_c)^t$, with $t \cong 1.28$.[44] Figure 5b shows the normalized σ values [$\sigma(L)/\sigma(2.5 \, \mu m)$] as a function of L for our three systems. The curves related to MoS_2 films and MoS_2–PDT networks collapse (i.e., overlap), proving that PDT exposure merely improves the already existing percolation paths (i.e., bonds) due to the healing of V_S, mainly located at the flake edges.[14] On the other hand, a distinct feature is unique to MoS_2–BDT networks: the different σ saturation level at long channels clearly indicates an additional benefit due to the network formation, which is ascribed to the creation of additional percolation paths as a result of the improved inter-flake electronic connectivity upon using π-conjugated linkers.

To investigate the role of additional percolation paths resulting from the network formation, we explore the influence of the concentration of functionalizing molecule (c_M) on the σ versus L dependence at three different c_M. We find a clear σ enhancement proportional to BDT c_M; in particular, upon increasing the c_M from 500 μM to 50 mM, the saturation level changes by $\approx 100\%$ because of the generation of new percolation paths within the channel (Figure 5c). Considering $\sigma_{\text{eff}} \equiv \sigma(L, c_M)$, it can be written

$$\sigma_k(L, c_M) = A_k(c_M)\left\{\left[p_k(c_M) - p_c\right]^t + bL^{-\beta}\right\} \qquad (4)$$

where $A_k(c_M)$ represents the average conductivity of a single bond, the index k refers to different devices, and b denotes the coefficient regulating the size dependence of σ in the percolation problem, which only depends on geometrical features. We claim, therefore, that the latter quantity does not significantly depend on c_M nor on k.

As reported in the Experimental Section, we can use the following approximate expression to describe the experimental data, defining the ratio $r_{k,k}(L, c_M, 0)$ between $\sigma_k(L, c_M)$ of MoS_2 samples before and after BDT functionalization

$$r_{k,k}(L, c_M, 0) \simeq a_{k,k}(c_M, 0)\frac{\left[p_k(c_M) - p_c\right]^t + bL^{-\beta}}{bL^{-\beta}} \qquad (5)$$
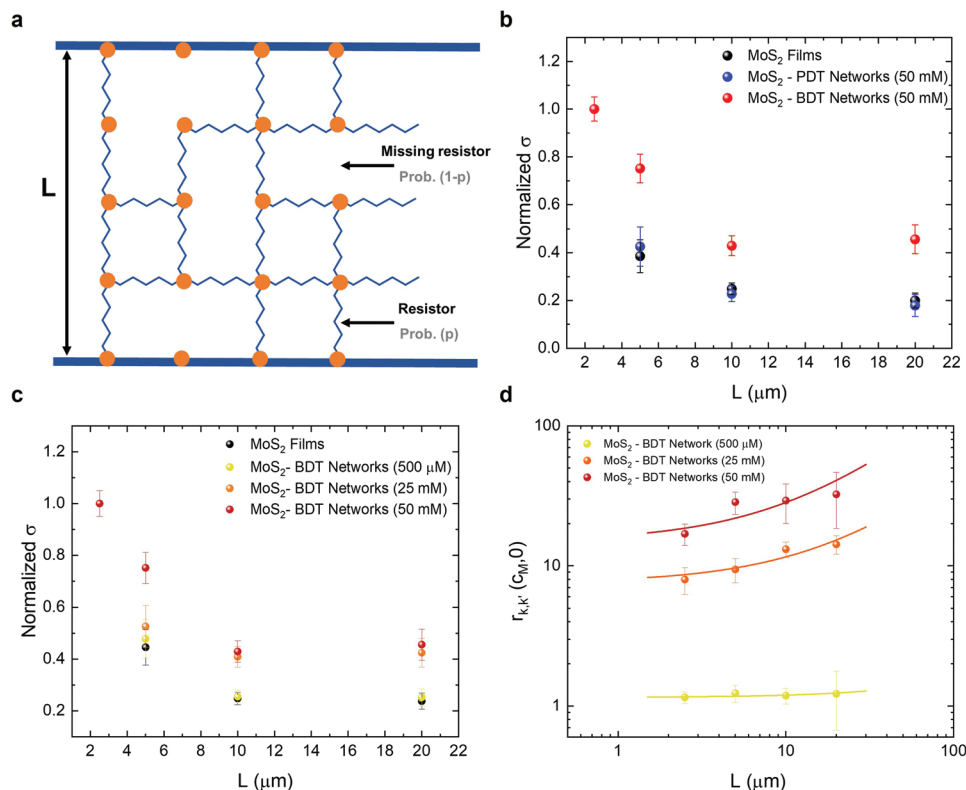

Figure 5. Percolation theory in MoS_2 films and covalent networks. a) Sketch of the random resistor network model, where p and $1 - p$ represent the probability of a resistor and missing resistor, respectively. b) Normalized σ versus L plot showing the critical $1/L$ trend for MoS_2 films and 50 mM-functionalized MoS_2–PDT and MoS_2–BDT networks. The normalized σ values at $L = 2.5 \, \mu m$ coincide for all systems. c) Normalized σ versus L plot for MoS_2–BDT networks as a function of BDT concentration, ranging from 500 μM to 50 mM. The normalized σ values at $L = 2.5 \, \mu m$ coincide for all systems. d) $r_{k,k'}(c_M, 0)$ versus L curves for MoS_2–BDT networks at three different values of c_M. The dots (with error bars) represent the experimental data, while the continuous lines are the analytic form Equation (5) with the fitted parameters $a_{k,k}(c_M, 0)$ and $p_k(c_M) - p_c$.

where $a_{k,k}(c_M,0) := A_k(c_M)/A_k(0)$ and with $b = 5.40\ \mu m^\beta$. The experimental determination of $r_{k,k'}(L,c_M,0)$ for three different values of c_M and the related analytic expressions are reported in Figure 5d. The two quantities $a_{k,k}(c_M,0)$ and $p_k(c_M) - p_c$ are obtained by best fit procedure where the data are proportionally weighted to their inverse squared experimental error. The results of the fitted parameters are shown in Table S8 (Supporting Information).

Figure 5d unambiguously demonstrates two different effects resulting from the BDT functionalization: i) the drastic increase of $a_{k,k}(c_M,0)$ with increasing c_M (highlighted by the overall value of $r_{k,k}(c_M,0)$), pointing out an improved bond conductivity; ii) the increase of $p(c_M) - p_c$ (associated with the upward bending of $r_{k,k'}(c_M,0)$ vs L curves), revealing the formation of additional bonds due to the improved interflake electronic connectivity. Both effects contribute to increasing the overall $\sigma(L, c_M)$.

3. Conclusions

Our multiscale investigation on the transport properties of covalent MoS_2 networks reveals hopping as the dominant charge-transport mechanism, unveiling the paramount role played by the chemical structure of the bridging linkers. The improved inter-flake electronic connectivity, exclusively provided by π-conjugated BDT linkers, is pointed out in the TLM analysis, where a quadratic dependence in the R_T versus L plots is observed for pristine MoS_2 films and MoS_2–PDT networks, unlike the ideal linear trend restored in MoS_2–BDT networks due to the successful bridging of adjacent flakes. Furthermore, in agreement with DFT calculations, our innovative percolation analysis, conducted for the first time on MoS_2 electrical devices, confirms the improvement of already existing percolation paths and the formation of additional ones in MoS_2–BDT networks. In conclusion, we provide an analytical protocol to elucidate the charge transport in TMD devices. Moreover, our findings reveal that the defect engineering using suitably designed dithiolated molecules represents a powerful strategy for harnessing the transport properties in covalent MoS_2 networks, paving the way to the fabrication of high-performance devices for printed electronics.

4. Experimental Section

MoS₂ Ink Preparation: MoS_2 inks were obtained by sonicating the respective powders in *N*-methyl-2-pyrrolidone (NMP). An initial concentration of 20 mg mL^{-1} was processed for 1 h in 80 mL of NMP using a tip horn sonicator (Sonics Vibra-cell VCX-750 ultrasonic processor) at 60% amplitude. The resulting dispersion was centrifuged at 3218g for 1 h using a Hettich Mickro 220R, after which the supernatant was discarded to remove potential contaminants from the starting powder. The sediment was then redispersed in fresh NMP and sonicated under the same conditions for 6 h. This process gave a polydisperse stock dispersion from which flakes could be size selected by centrifugation. For each material, the polydisperse stock was first centrifuged at 106.4g for 90 min to remove the largest aggregates, with the sediment retained for future exfoliation. The supernatant was then centrifuged at 425g for 90 min to separate the smaller flakes. Finally, this sediment was redispersed in 30 mL of 2-propanol.

MoS₂ Ink Characterization: The as-exfoliated MoS_2 flakes, both in solution and solid state, were characterized by spectroscopic and morphological analysis. Detailed information was reported below.

MoS₂ Ink Characterization—UV–Vis Spectroscopy: UV–vis spectra were recorded under ambient conditions on a Perkin Elmer 1050 spectrometer equipped with an integrating sphere (150 mm) attachment, using quartz cuvettes with an optical path length of 4 mm. The concentration of the MoS_2 ink could be extracted from the UV–vis spectra by means of the Lambert–Beer law, using the extinction coefficient at 345 nm (69 mL mg^{-1} cm^{-1}) where it was relatively invariant across the lateral size and thickness of MoS_2 flakes.[46]

MoS₂ Ink Characterization—Raman Spectroscopy: Raman spectra were recorded under ambient conditions with a Renishaw inVia spectrometer at 532 nm with a 100× objective (numerical aperture 0.85). The power was kept below 1 mW to avoid local heating and damage effects.

MoS₂ Ink Characterization—Scanning Electron Microscopy (SEM): SEM images were captured using a Zeiss Ultra Plus, operating with a gun pressure $\approx 10^{-8}$ mbar and chamber pressure $\approx 10^{-6}$ mbar, working at 2–5 kV.

MoS₂ Ink Characterization—Atomic Force Microscopy (AFM): AFM images were taken with a Bruker Dimension Icon microscope under ambient conditions, operating in tapping mode and using TESPA-V2 tips with spring constant $k = 42$ N m^{-1}. The images were captured at a scan rate equal to 1.0 Hz with 1024 lines per image.

Electrical Device Fabrication: The source, drain, and gate electrodes of the device were patterned by photolithography (AZ1505 photoresist and MIF326 developer, MicroChemicals) using Microtech LW405B laser writer. 5 nm of chromium and 40 nm of gold were thermally evaporated with Plassys MEB 300, followed by liftoff in warm (50 °C) acetone for 90 min to output the final electrodes. Finally, the devices were rinsed with acetone and 2-propanol to remove photoresist residues. The device geometry displayed 22 interdigitated electrodes having channel lengths from 2.5 to 20 μm and channel width of 10 000 μm, while the area of the coplanar gate electrode was ≈ 1 mm². The very same protocol was used for both rigid (Si/SiO₂) and flexible (polyimide) substrates.

MoS₂ Ink Deposition: Before deposition, the electrode-patterned Si/SiO₂ substrates (1.5 × 1.5 cm²) were cleaned by ultrasonication in acetone and 2-propanol for 10 min, each. Subsequently, they were heated on a hot plate at 80 °C, with their electrodes covered by blue masking tape. Then, 10 mL of MoS_2 ink (concentration ≈ 0.2 mg mL^{-1}) was sprayed on the substrate using a commercial airbrush gun (Timbertech ABPST01), with needle and nozzle diameter equal to 0.3 mm, supplied by compressed nitrogen at 1 bar. The distance between the nozzle tip and the substrate was kept at ≈ 20 cm.

Stylus Profilometry: The thickness of MoS_2 films was measured with a KLA-Tencor Alpha-Step IQ profilometer, operating under ambient conditions. All films showed a thickness of 500 ± 50 nm.

Functionalization Reaction: Upon deposition, the MoS_2 thin films were moved under N₂-controlled atmosphere (i.e., glovebox) for the following functionalization steps: i) sample immersion within BDT/PDT 50 mM solution in anhydrous hexane for 48 h (dark) inside a sealed container, ii) spin-rinsing with anhydrous hexane (5 mL, 4000 rpm, acceleration 4000 rpm s^{-1}, 60 s), and iii) spin-drying at the very same conditions. The preparation of BDT and PDT solutions (e.g., powder weighing, dissolution) was carried out under inert atmosphere to avoid thiol oxidation reactions induced by impurities.

THz Spectroscopy: The photoconductivity ($\Delta\sigma_{ph}$) measurements were performed by using an optical-pump THz-probe setup, which was driven by a Ti:sapphire laser amplifier system providing ≈ 50 fs laser pulses with a central wavelength of 800 nm. A pair of ZnTe nonlinear crystals were used for the generation and detection of THz electric field, which provided frequency information ranging from 0.4 to 2.5 THz. For optical-pump excitations, frequency-doubled wavelength (400 nm) generated from the fundamental wavelength (800 nm), by using a BiB₃O₆ crystal, was employed. The samples were placed under vacuum conditions ($\approx 10^{-4}$ mbar) during measurements.

For the thin-film geometry, the Fourier transformation was used to convert the relative change of the THz electric field from time to frequency domain and further quantify the complex $\Delta\sigma_{ph}$ spectra based on the thin-film approximation[19]

$$\Delta\sigma_{ph}(\omega) = -\frac{n_1 + n_2}{Z_0 t_{ex}}\frac{\Delta E(\omega)}{E(\omega)} \tag{6}$$

where $Z_0 = 377 \, \Omega$ is the impedance of free space, t_{ex} is the excitation thickness, n_1 and n_2 are the refractive indices of the media before and after the sample, respectively.

To analyze the frequency-domain conductivity spectra, the Drude–Smith (DS) model was applied. The DS model described the transport of free charges experiencing backscattering processes due to, for instance, defects and/or structural deformations. The DS equation read

$$\sigma_{ph}(\omega) = \frac{\varepsilon_0 \omega_P^2 \tau}{1 - i\omega\tau}\left(1 + \frac{c}{1 - i\omega\tau}\right), \text{ with } \omega_P^2 = \frac{e^2 N}{\varepsilon_0 m^*} \tag{7}$$

where c represents the backscattering probability for carrier transport, whose value ranged from 0 (free charge) to −1 (preferential backscattering). τ, ω_p, ε_0, e, and m^* are the effective carrier momentum scattering time, plasma frequency, vacuum permittivity, elementary charge, and carrier effective mass, respectively.

To analyze the scattering times, the overall carrier scattering rate ($k_{overall}$, the inverse of scattering time) was considered taking into account the contributions from the carrier–phonon scattering (k_{phonon}) and the carrier–defect scattering (k_{defect}), following the Matthiessen's law[47]

$$k_{overall} = k_{defect} \times T^{-3/2} + k_{phonon} \times T^{\alpha} \tag{8}$$

where α is the power index. During the fitting process, identical k_{phonon} was assumed for both MoS$_2$ films and MoS$_2$–BDT networks. The fit gave: $\alpha = 0.19$ and $k_{phonon} = 4.9$ THz for both MoS$_2$ films and MoS$_2$–BDT networks, and $k_{defect} = 6.96$ THz for MoS$_2$ films and $k_{defect} = 4.03$ THz for MoS$_2$–BDT networks.

Charge-Transport Analysis: The electrical devices were measured in two-probe configuration in a customized Janis cryogenic probe station, connected to a semiconductor parameter analyzer (Keithley 4200A SCS). The chamber pressure was kept at $\approx 10^{-7}$ mbar. A Sumitomo RDK-408D2 cryogen-free closed cycle was thermally anchored to the copper sample holder and the temperature measurements were performed within the T range 340–5K. To enable statistical analysis, 48 identical devices were produced and subjected to electrical characterization.

Charge-Transport Analysis—Calculation of Localization and Average Hopping Length: For ES-VRH, the localization length ξ_{ES} was related to the characteristic temperature T_0 according to the following equation[48]

$$\xi_{ES} = \frac{2.8e^2}{\pi k_B \varepsilon \varepsilon_0 T_0} \tag{9}$$

from which the average hopping distance $R_{ES\text{-}VRH}$ was calculated as

$$R_{ES-VRH} = 0.25\left(\frac{T_0}{T}\right)^{1/2} \xi_{ES} \tag{10}$$

For 3D Mott VRH, the localization length $\xi_{3D\text{-}VRH}$ was related to the characteristic temperature T_0 as[16,18,49]

$$\xi_{3D-VRH} = \frac{24}{\pi k_B \varepsilon_0 \varepsilon_r T_0 N(E_F)} \tag{11}$$

from which the average hopping distance $R_{3D\text{-}VRH}$ was calculated as

$$R_{3D-VRH} = \frac{3}{8}\left(\frac{T_0}{T}\right)^{1/4} \xi_{3D-VRH} F_0 \tag{12}$$

where F_0 is a correction factor (equal to 1 when $T \ll T_0$).

In the case of the NNH, the average hopping distance R_{NNH} was related to the activation energy by the following equation

$$R_{NNH} = \left[N(E_F)E_a\right]^{1/3} \tag{13}$$

The DOS at the Fermi level [$N(E_F)$] was extrapolated from DFT calculations for the MoS$_2$–BDT and MoS$_2$–PDT networks.

The T_0 related to each hopping mechanism was extrapolated from the linear fit of the $\ln(\sigma)$ versus $T^{-\alpha}$ curve, as reported in Section S3 (Supporting Information). Considering the T_0 for the three systems, the hopping models were always valid within the whole T range, being

$T \ll T_0$. The obtained values of ξ and R_{hop} were in good agreement with previous results reported in literature.[15,17]

DFT Calculations: DFT calculations were performed using the projector-augmented wave basis set using the Vienna Ab initio Simulation Package (VASP) code,[50,51] with the exchange and correlation effects treated at the Perdew–Burke–Ernzerhof (PBE) level.[52,53] Dispersion forces by Grimme correction (PBE + D2)[52,53] and dipole moment correction along the c-axis (direction perpendicular to the MoS$_2$ surface) were incorporated with a kinetic energy cutoff of 600 eV. Calculations were performed on MoS$_2$ crystals in their bulk form, replicated 4×4 times, using a Monkhorst–Pack sampling of $4 \times 4 \times 4$ for the Brillouin zone integration for all geometry optimizations. The geometries of MoS$_2$ crystals in their pristine, defective (with sulfur vacancies), and BDT/PDT network forms were fully optimized, after which self-consistent field (SCF) calculations were performed at the generalized gradient approximation (GGA)/PBE and HSE06 levels of theory using a dense K-point grid of $6 \times 6 \times 6$ and $3 \times 3 \times 3$, respectively. CDD plots were computed using $CDD = CD_{MoS_2+Mol} - CD_{MoS_2} - CD_{Mol}$, where CD_{MoS_2+Mol} is the charge density of BDT/PDT (Mol) covalent networks, CD_{MoS_2} and CD_{Mol} are the charge densities of the isolated defective MoS$_2$ surface and BDT/PDT molecules, respectively.

Electrical Characterization: The performance of electrical devices based on MoS$_2$ films and networks was evaluated by their transfer characteristics (I_{ds} vs V_{gs} curves), using a coplanar Au-gate electrode covered with 75 µL of EMI–TFSI as ionic liquid. The source–drain current (I_{ds}) was recorded sweeping the gate voltage (V_{gs}) from −2.5 to +2.5 V, at a source–drain bias $V_{ds} = -0.1$ V. All electrical measurements were carried out in dark and under inert atmosphere (N$_2$) using a Keithley 2636 A Source Meter unit. To enable statistical analysis, 24 identical devices were produced and subjected to electrical characterization. The TLM analysis was performed with the same experimental setup on devices fabricated with prepatterned substrates of channel lengths ranging from 2.5 to 20 µm. The R versus L curves of MoS$_2$ films and networks were fitted using allometric and linear equations, respectively.

To enable statistical analysis, 60 identical devices were produced and characterized.

Percolation Theory: Starting from the expression

$$\sigma_k(L, c_M) = A_k(c_M)\left\{\left[p_k(c_M) - p_c\right]^t + bL^{-\beta}\right\} \tag{14}$$

the ratio between measurements in two samples k, k′ at different concentrations c_M and $c_M′$ read

$$r_{k,k'}(L, c_M, c_M') = a_{k,k'}(c_M, c_M')\frac{\left[p_k(c_M) - p_c\right]^t + bL^{-\beta}}{\left[p_{k'}(c_M') - p_c\right]^t + bL^{-\beta}} \tag{15}$$

where $a_{k,k'}(c_M, c_M') := A_k(c_M)/A_{k'}(c_M')$. As a function of L, this quantity was a sigmoid-like monotonic function, starting from a plateau value $a_{k,k'}(c_M, c_M')$ at small L and then reaching a constant value $a_{k,k'}[p_k(c_M) - p_c]^t/[p_{k'}(c_M') - p_c]^t$ for large L. Considering the ratios between different MoS$_2$ films

$$r_{k,k'}(L, 0, 0) = a_{k,k'}(0,0)\frac{\left[p_k(0) - p_c\right]^t + bL^{-\beta}}{\left[p_{k'}(0) - p_c\right]^t + bL^{-\beta}} \tag{16}$$

no monotonic dependence on L within errors was observed, meaning that $p_k(0) \simeq p_{k'}(0)$. Hence, although different MoS$_2$ films had different electrical conductivities (related to the deposition steps), these variations must be considered as an effect of the different values for the average bond conductivity $A_k(0)$. The σ ratio of the MoS$_2$ sample before and after the BDT functionalization was defined as

$$r_{k,k}(L, c_M, 0) \simeq a_{k,k}(c_M, 0)\frac{\left[p_k(c_M) - p_c\right]^t + bL^{-\beta}}{\left[p_k(0) - p_c\right]^t + bL^{-\beta}} \tag{17}$$

All the quantities in the equation must be dimensionless, therefore $b = \mu m^\beta$ to be consistent with L expressed in µm. Fitting the experimental data, similar b values were observed for all samples, so it was set $b = 5.40 \, \mu m^\beta$ calculated as their mean value.

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Furthermore, the term $(p_k(0) - p_c)^t$, for every k, was negligible compared to $bL^{-\beta}$ for the L taken into account. Thus, the approximate expression

$$r_{k,k}(L, c_M, 0) \simeq a_{k,k}(c_M, 0) \frac{\left[p_k(c_M) - p_c\right]^t + bL^{-\beta}}{bL^{-\beta}} \tag{18}$$

with $b = 5.40~\mu m^\beta$, could be used to describe the experimental data. It was worth mentioning that such a value of b indicated that finite-size effects were significant in the L range under analysis. The importance of finite-size effects was also evident from the lack of saturation in $r_{k,k}(c_M, 0)$ versus L curves, expected from the exact expression.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

S.I., F.U., and P.S. conceived the experiments and designed the study. S.I. and F.U. performed the electrical characterizations and charge-transport analysis. W.Z., M.B., and H.I.W. carried out the THz spectral analysis. O.M. and F.C. developed the percolation theory related to the electrical devices. C.V. performed the deposition of MoS_2 ink via spray coating. A.G.K. and J.N.C. produced and characterized the solution-processed MoS_2 ink. S.M.G. and D.B. performed and analyzed the DFT calculations. All authors discussed the results and contributed to data interpretation. S.I., F.U., and P.S. cowrote the paper with input from all coauthors.

Data Availability Statement

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

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