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Towards scalable high-performance molecular electronics devices based on diketopyrrolopyrrole derivatives

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Large-area molecular junctions offer a promising pathway toward the scalable implementation of molecular electronic devices, where charge transport is strongly governed by molecular structure and supramolecular organization. In this work, two diketopyrrolopyrrole (DPP) derivatives featuring tailored alkyl chain lengths designed to isolate the DPP moiety from the anchor groups, are used to form well-ordered Langmuir–Blodgett (LB) films. By bridging the gap between single-molecule behavior and collective transport in large-area devices, molecular junctions were first characterized using the ‘scanning tunneling microscopy (STM) touch-to-contact’ method. These junctions exhibit higher conductance than conventional single molecule *I*(*s*) measurements, attributed to intermolecular charge-transfer processes enabled by the ordered LB assemblies. Consistent with this enhanced conductance, low transition voltages (V_{trans}) indicate favorable alignment between the metal electrode Fermi level and the frontier molecular orbitals. To assess device-relevant performance, large-area molecular junctions were fabricated using Eutectic Gallium–Indium (EGaIn) alloy as a soft top electrode. These junctions exhibit high yield and reproducibility, confirming the formation of robust and high-quality junctions that mirror the transport behavior observed at the single-molecule scale. Together, these results establish a consistent transport picture across both small- and large-area junctions identifying the DPP moiety as a highly effective molecular wire. This effectiveness stems from the capability of these DPP derivatives to form well-ordered films exhibiting intermolecular charge-transfer processes, which, combined with a favorable energy-level alignment with the electrodes, ultimately results in high device conductance.

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1. Introduction

The main premise in the field of molecular electronics is that tailored molecules, synthesized with the desired molecular structure, can perform in the same manner as classical electronic components such as wires, switches, rectifiers or transistors.^{1–6} The use of molecules as building blocks in electronic devices may not only overcome the size limitations of current semiconductor technology, but also allow novel functionalities arising from intrinsic molecular properties to be exploited and fine-tuned

depending on the desired application.⁷ Single-molecule junctions provide key insight into the electrical properties of molecules, and more importantly, enable correlations between molecular structure, electrical properties and molecule-metal interfaces, which are essential for progress toward the fabrication of molecular devices with the desired functionality.^{7–10} Nevertheless, single-molecule junctions are accompanied by issues related to the reproducibility and stability of the junctions, which arise from differences and fluctuations in molecular conformation, the electrode-anchor contact geometry, or the electrode surface geometry within each junction.^{7,11–14} Although several strategies have been developed to address these issues,^{15–21} the establishment of a technology for the fabrication of single-molecule devices remains a challenge. In this context, ‘large-area’ ensemble or monolayer film structures are more likely to find implementation in practical device structures.^{13,22} Fabrication of large-area devices involves the deposition of a monolayer onto a bottom electrode to form high-quality and reproducible assemblies, followed by the

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deposition of a top electrode onto the molecular monolayer without damaging it, forming pinholes or short-circuits, or altering or contaminating the interface.¹³ Charge transfer in large-area junctions depends not only on the structure and chemical conformation of the molecular skeleton but also on the interactions of the anchoring groups with the electrodes and the surrounding molecular environment, as well as on the packing, ordering, and number of molecules in the junction.^{22–25} However, strong coupling effects and other intermolecular interactions can affect the properties of the individual molecules and/or the device in these assemblies.^{26–28} Given the promising perspective of large-area molecular devices, efforts to improve and control the electrical properties of these molecular junctions remain a key challenge in the development of future molecular electronic devices, where molecular structure represents one of the main parameters that largely defines the electronic functionality of the molecular device.^{7,8,29,30} In this context, diketopyrrolopyrrole (DPP) derivatives have been widely used in organic electronics as semiconductors in solar cells, field-effect transistors or in light-emitting diodes,^{31–37} due to the versatility and excellent charge-transport properties of the DPP moiety. This arises from its highly conjugated donor–acceptor–donor (D–A–D) architecture, where the strong acceptor DPP moiety can be stabilized by two donor groups,

which can have a subtle influence on properties such as absorption, emission, energy levels, or charge carrier mobility.^{38,39} Despite this, the use of the DPP moiety in single-molecule junctions has received relatively little consideration to date^{40–45} and has been largely unexplored in large-area junctions to the best of our knowledge. Therefore, to evaluate the role of the DPP moiety in large-area molecular electronic devices, we report the formation of Langmuir and Langmuir–Blodgett (LB) films of two bis-thiophene-DPP derivatives in which the DPP moiety is isolated from the anchoring groups by alkyl chains of different lengths at either end of the molecule ($(\text{CH}_2)_n$ with $n = 4$ or 6) (Fig. 1a). The electrical characterization of these LB films confirms that thiophene-DPP moiety is an excellent candidate to be used as backbone in the construction of future large-area molecular electronic devices as these large-area junctions show a higher conductance than single-molecule junctions and V_{trans} values lower than or comparable to those obtained for conjugated self-assembled molecular wires.

2. Experimental section

2.1. Synthesis of compounds

Synthesis and characterization of compounds **1** and **2** are described in detail in SI.

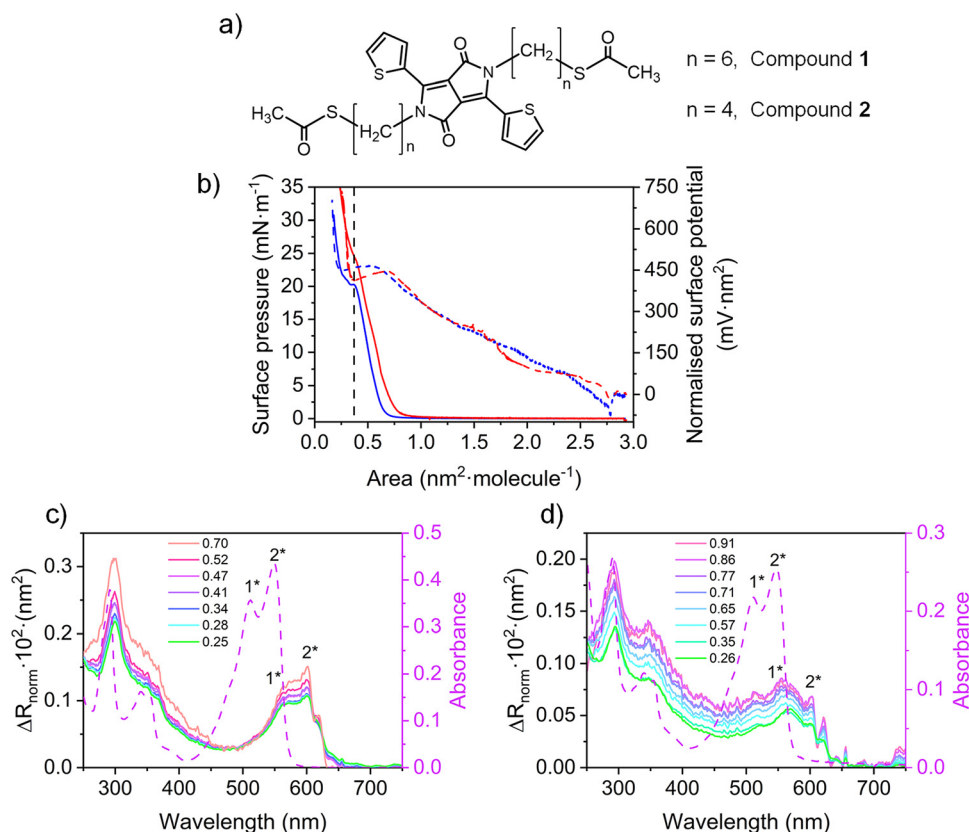


Fig. 1 (a) Molecular structure of compounds **1** and **2**. (b) Surface pressure (π –A, solid lines) and normalized surface potential (ΔV_n –A, dashed lines) vs. area per molecule isotherms for **1** (blue lines) and **2** (red lines). Normalized UV-vis reflection spectra recorded at the air–water interphase at the indicated area per molecule in nm^2 (c) compound **1** and (d) compound **2**. The spectrum of a 1×10^{-5} M solution in CHCl_3 of both compounds (dashed purple line) is also shown for comparison. Dashed black line in (b) shows the point from which the formation of a multi-layered structure occurs.

2.2. Film fabrication and characterization

A Nima Teflon trough ($720 \times 100 \text{ mm}^2$) located in a cleanroom maintained at constant temperature ($20 \pm 1^\circ\text{C}$) was used to prepare the molecular films on a pure water sub-phase (Millipore Milli-Q purification system, resistivity $18.2 \text{ M}\Omega \text{ cm}$) using a Wilhelmy paper-plate pressure sensor to determine the surface pressure (π). $1 \times 10^{-5} \text{ M}$ solutions of **1** and **2** in chloroform (HPLC grade purchased from LabScan (99.8%)) were used to fabricate the Langmuir films with an initial area per molecule of $2.9 \text{ nm}^2 \text{ molecule}^{-1}$. Once the solution was spread on the water sub-phase and before starting the compression of the film at a constant compression rate of $0.02 \text{ nm}^2 \text{ molecule}^{-1} \text{ min}^{-1}$, the chloroform was allowed to evaporate over 15 minutes. The isotherms were highly reproducible under these experimental conditions. Surface potential isotherms (ΔV -A) were recorded simultaneously to π -A isotherms using a Kelvin Probe provided by Nanofilm Technologie. Meanwhile, direct visualization of the monolayers at the air-water interface was carried out by a commercial mini-Brewster Angle Microscope (mini-BAM), from Nanofilm Technologie, and reflection spectra of the Langmuir films upon compression⁴⁶ by using a commercial UV-vis reflection spectrophotometer, with a light source FiberLight DTM 6/50 and an absolute wavelength accuracy $<0.3 \text{ nm}$ and a resolution (Raylight-criterion) $>3 \text{ nm}$.

The vertical dipping method (dipping speed of 3 mm min^{-1}) was used to fabricate Langmuir-Blodgett (LB) monolayers onto solid supports at a constant surface pressure. UV-vis spectra of the LB films transferred onto a quartz substrate oriented perpendicular to the incident beam were recorded with a Varian Cary 50 spectrophotometer. Atomic force microscopy (AFM) images were acquired under ambient air conditions with a Bruker Multimode 8 microscope with a Nanoscope V control unit at a scan rate of 1 Hz in tapping mode using RTESPA-150 AFM probes (provided by Bruker, $90\text{--}210 \text{ kHz}$ resonant frequency, 5 N m^{-1} spring constant, nominal tip radius of 8 nm).

2.3. Electrical characterization

An Agilent 5500 SPM microscope using the 'scanning tunneling microscopy (STM) touch-to-contact' method⁴⁷ or the $I(s)$ method⁴⁸ was used to determine the electrical properties of the LB films or the single molecule conductance, respectively. The 'STM touch-to-contact' method was employed to record I - V curves with an atomically sharp STM tip contacting the monolayer. The $I(s)$ method was used for registering hundreds of events (at a given set-point current and bias voltage) showing current steps associated with the formation of molecular bridges, which were analyzed statistically in the form of histogram plots to determine the single molecule conductance. Molecular adsorption was achieved by immersion of the substrates in a solution of **1** or **2** in CHCl_3 (0.1 mM) for about 60 s . After adsorption, the samples were washed in ethanol and then blown dry in a stream of nitrogen. All measurements were conducted in air. Additionally, the $I(s)$ method was also used to determine the conductance of molecules assembled into LB films of **1**.^{49–52} In this case, the junctions were formed by placing the atomically

sharp gold STM tip at a given distance enough to penetrate the monolayer ($U_t = 0.6 \text{ V}$ and $I_0 = 10 \text{ nA}$). Once the proper distance was achieved, the feedback was disabled, and the STM tip was retracted while keeping a constant x - y position. Under these conditions, one (or more) molecules linked between the STM tip and monolayer and the current as a function of distance was recorded until this linkage(s) breaks. This procedure resulted in a current plateau followed by a step in the $I(s)$ retraction curve, which was attributed to conduction through a molecular bridge simultaneously bound to the tip and the substrate. These current-distance [$I(s)$] curves were statistically analyzed in the form of histogram (by adding all the current (or conductance) data points from *ca.* 140 current *versus* distance curves showing a discernible plateau. As a consequence, the molecule (or molecules) initially trapped within the junction must presumably tilt toward the horizontal in order to compensate for the vertical approach of the tip and, then, during measurement, these are "lifted" until the molecule bridge(s) breaks. Therefore, this method of measurement is inherently destructive for the monolayer structure as it involves penetration of the tip into the film, leading to disruption of possible intermolecular interactions in the monolayer.

2.3.1. Eutectic gallium-indium (EGaIn) measurements. J - V characteristics of the junctions with geometry Au-1 or 2 LB films//GaOx/EGaIn were measured by top-contacting the LB film with an EGaIn tip shaped as a cone. A conical liquid-metal tip was formed by dispensing a small droplet from a syringe needle, contacting it with a clean gold surface, and retracting it. To ensure a smooth and reproducible interface, the tip was gently contacted three times with a flat SiO_2/Si wafer, then positioned above the monolayer and slowly approached using micromanipulators under optical monitoring.

After measuring the geometrical contact diameter from the optical image of the junction (a representative photograph is shown in Fig. S14), J - V characteristics were recorded by biasing the GaOx/EGaIn top electrode while the Au substrate was grounded through a tungsten microprobe mounted on a micromanipulator in a probe station. Electrical measurements were acquired using a Keithley 2604B electrometer, applying a voltage sweep defined as $0 \rightarrow +0.5 \text{ V} \rightarrow -0.5 \text{ V} \rightarrow 0$ in steps of 0.025 V , while continuously recording the corresponding current density response. The recording of each J - V measurement was preceded by a pre-pulse stabilization period of 2 s before data acquisition. A delay of 20 ms was applied at each step to allow interfacial equilibration, followed by a 50 ms dwell time for current sampling.

Although the true effective electrical contact area is not directly measurable, the extracted current densities can be treated as relative figures of merit, only allowing statistically robust comparisons between samples measured under identical systematic experimental steps. The measured geometrical contact areas fall in the range of $600\text{--}1350 \mu\text{m}^2$.

All the measurements were performed under controlled ambient conditions (average $23.6\text{--}25.2^\circ\text{C}$, $40\text{--}44\% \text{ RH}$) to minimize environmental contributions to current variability.

For each sample, a minimum of six freshly prepared EGaIn junctions were formed, and several spatially separated regions

of the LB films were probed with each tip. For each junction, 10 consecutive complete sweeps were collected, providing statistically robust datasets. Current density curves were obtained using the measured geometrical area of the EGaIn junction captured with a camera.

3. Results and discussion

3.1. Langmuir and Langmuir–Blodgett films fabrication

The concentration and volume of the spreading solution can influence the formation of Langmuir films at the air–water interface.²³ Therefore, a preliminary study was undertaken to obtain reproducible isotherms for both compounds. This survey concluded that only solutions with a concentration lower than 1×10^{-5} M produced reproducible surface pressure *vs.* area per molecule (π -A) isotherms (Fig. 1b, solid lines) for both compounds. These isotherms showed a gas phase region from 2.90 to 0.60–0.70 nm² molecule⁻¹, in which the surface pressure remains close to zero. At *ca.* 0.60–0.70 nm² molecule⁻¹, a sharp increase in the π -A isotherms occurred, followed by a continuous increase in the surface pressure maintaining a constant slope, a characteristic feature indicating a transition to a more condensed phase. Upon further compression up to 0.40–0.45 nm² molecule⁻¹, a change in the slope to a flatter region indicated the transition of the monolayer to a more condensed phase, and the subsequent increase in surface pressure upon compression revealed the formation of a multi-layered structure, as demonstrated by atomic force microscopy (AFM) (Fig. S1 in SI). Fig. 1b also shows (dashed lines), the normalized surface potential *vs.* area per molecule, ΔV_n (surface potential multiplied by the area per molecule). These isotherms complement the information provided by the surface pressure-area per molecule isotherms, as the surface potential is usually more sensitive to molecular ordering and can reveal further details about the degree of molecular organization. For both compounds, the normalized surface potential increased steadily from 2.80 to 0.60–0.70 nm² molecule⁻¹. This behavior was attributed to the coalescence of domains into a more condensed phase at the interface, where attractive intermolecular forces (*e.g.*, π - π or van der Waals interactions) between neighboring molecules are maximized upon compression. The subsequent plateau in both cases, is attributed to the reorientation of the thiol groups and water molecules at the interface.¹⁹ Further compression of the monolayers caused a sudden increase in the gradient of the normalized surface potential slope, associated with the formation of more compact multi-layered structures.

Changes in the molecular organization of both compounds upon compression were examined by *in situ* UV-vis reflection spectroscopy under normal incidence with unpolarized light (Fig. 1c and d). The normalized reflection spectra, ΔR_n ($=\Delta R \times$ area per molecule) showed bands at *ca.* 300 and 350 nm attributed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively, of the DPP and thiophene moieties, and a broad dual band at 560 and 600 nm due to the $\pi \rightarrow \pi^*$ intramolecular charge-transfer

(ICT) from the thiophenes to the DPP.⁵³ Importantly, the intensity of these bands decreased upon compression, suggesting a reorientation of the dipolar transition moments (all confined in the thiophene-DPP (T-DPP) moiety)¹⁶ to a more vertical position with respect to the air–water surface.⁴⁶ Notably, the ICT dual band at 560 and 600 nm showed a considerable red shift (*ca.* 50 nm) relative to the spectrum in solution, suggesting intermolecular charge-transfer between the T-DPP moieties of neighboring molecules.^{54–56} Only a slight shift was observed for the other bands. The well-known tendency of the T-DPP derivatives to crystallize has been reported and explained by the absence of repulsive interactions between the thiophene and the DPP moiety, which favors the in-plane packing of the molecules.⁵⁷ Additionally, the alkyl chains present in both compounds favor the planarity of the T-DPP due to their conformational flexibility and near absence of steric hindrance, enhancing the formation of 2D aggregates.⁵³ Brewster angle microscopy (BAM) images were recorded at different stages of compression as illustrated in Fig. S2 and S3 for **1** and **2**, respectively. These images revealed the formation of homogeneous films at the air–water interface and an increase in brightness upon compression, confirming the progressive movement of the molecules to a more upright orientation with respect to the water surface.

Once high-quality Langmuir films were formed at the air–water interphase, these were transferred onto solid supports to give substrate-supported Langmuir–Blodgett films. This was achieved using the vertical dipping method with the substrates initially immersed in the water subphase. LB films at different surface pressures for both compounds were prepared on gold-on-mica substrates, and their morphology was analyzed by AFM (see SI for further details). Films transferred at a surface pressure of 7 mN m⁻¹ for **1** and at 12 mN m⁻¹ for **2** showed homogeneous monolayers, practically free of holes or three-dimensional defects, where the Au terraces can even be distinguished underneath the film and with very low root mean square (RMS) surface roughness (0.18 and 0.26 nm for **1** and **2**, respectively), as reported in Fig. 2. These surface pressures were therefore selected as the optimal transfer conditions. LB films of **1** were also transferred onto a quartz substrate at 7 mN m⁻¹ and the UV-Vis spectrum was recorded to gain further details concerning the molecular organization in the film (Fig. S6). The spectrum displayed a broadly similar shape to the reflection spectra obtained at the air–water interface at the same surface pressure but with lower apparent molar absorptivity. This pointed to a rearrangement of the T-DPP moiety to a more upright orientation with respect to the substrate during the transfer process, as supported by quartz crystal microbalance (QCM) measurements where a slight increase in the surface coverage for a LB film was observed relative to a Langmuir film of **1** at the air–water interface at a surface pressure of 7 mN m⁻¹ (2.65×10^{14} *vs.* 2.23×10^{14} molecules cm⁻²); see SI for more details.

X-ray photoelectron spectroscopy (XPS) was used to probe the binding interactions between both compounds and the gold substrate. Analysis of the spectra shown in Fig. S8

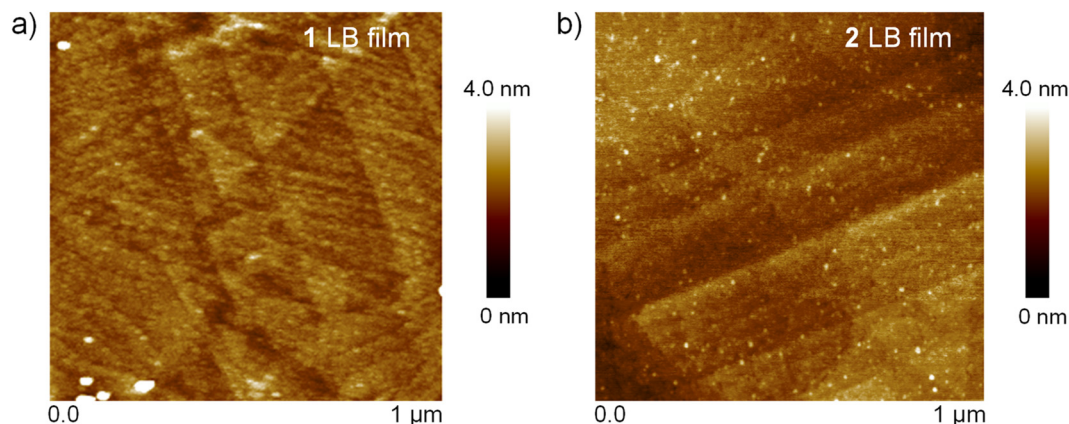


Fig. 2 Topographic AFM images of a LB film of (a) **1** transferred at 7 mN m^{-1} and (b) **2** at 12 mN m^{-1} onto gold on mica.

indicated that, in **1** and **2** LB films, molecules were oriented normal to the substrate surface and anchored to the substrate through one of the thioacetate groups, leaving the other thioacetate group available for contact the top electrode (see SI for further details).

3.2. Electrical properties

3.2.1. ‘Scanning tunneling microscopy (STM) touch-to-contact’ method. The “STM touch-to-contact” method⁴⁷ was used to determine the electrical properties of the LB films described above. In this method, an atomically sharp STM tip is positioned on top of the monolayer to establish contact, while avoiding both tip penetration into the film and the presence of any significant gap between the STM tip and the monolayer, thereby forming single-molecule junctions with individual molecules within substrate-supported monolayers. In the absence of intermolecular interactions, conductance values obtained by the “STM touch-to-contact” method are in excellent agreement with those measured for ‘conventional’ single-molecule junctions formed from low-coverage molecular films and the $I(s)$ technique.^{58–60} This reveals that only a single molecule within substrate-supported monolayers is contacted during the “STM touch-to-contact” measurements. However, to locate the STM tip just above the monolayer, the thickness of the LB films must be determined by an independent method. The thicknesses of the LB films of **1** and **2** transferred at 7 and 12 mN m^{-1} , respectively, were estimated to be 1.0 and 0.9 nm, as determined by scratching the LB films with the AFM tip in contact mode (Fig. S9 and S10 and SI for details). These thicknesses are smaller than the estimated molecular lengths (from sulphur to sulphur), as calculated using the molecular modelling program Spartan for a full extended of the alkyl chains (2.2 and 1.7 nm for **1** and **2**, respectively). This indicates a remarkable tilt angle of the molecules with respect to the substrate (27° and 32° , respectively), which likely favours intermolecular charge transfer from the thiophene units to the DPP moieties of neighboring molecules (Fig. 3a), as evidenced by the *ca.* 50 nm-red shift in the UV-vis absorption spectra (Fig. 1c and d). This behavior may also be associated with the

formation of gauche conformations of the alkyl chains. On the other hand, the similar thickness of both films, despite **2** being *ca.* 0.5 nm shorter than **1**, is attributed to a higher contribution of gauche conformations in the molecules of **1** within the monolayer. This is consistent with the longer alkyl chains in **1** (Fig. 1a).⁶¹ Once the thicknesses were determined, a calibration of the STM tip-substrate separation to an absolute tip-to-substrate distance (by relating the STM set-point parameters, set-point current, I_0 , and tip bias, U_t) was required to position the STM tip on top of the monolayers.^{47,59} For this, a series of current-distance retraction scans ($I(s)$ curves) displaying an exponential decay, associated with the absence of molecular junction formation, were recorded using a set-point current of $I_0 = 60 \text{ nA}$ and $U_t = 0.6 \text{ V}$ to ensure that the tip was embedded into the LB film before the retraction. The current decay $d \ln I / ds$ within the LB film was estimated using these $I(s)$ curves by plotting $\ln I$ vs. s . Note that the typically curved region at the beginning of the $\ln I$ vs. s retraction scan, which arises from an initial inertia in the piezo movement, was omitted from the analysis. Average slopes of $8.75 \pm 0.05 \text{ nm}^{-1}$ for **1** and of $9.25 \pm 0.07 \text{ nm}^{-1}$ for **2** were obtained (Fig. S11). With these values and assuming that the conductance when the STM tip makes atomic contact with the substrate is G_0 ($G_0 = 2e^2/h = 77.5 \text{ } \mu\text{S}$), the set-point parameters to locate the STM tip just above the LB films could be estimated using the following eqn (1):

$$s = \frac{\ln(G_0 \times U_t / I_0)}{d \ln(I) / ds} \quad (1)$$

Accordingly, using set-point parameters $I_0 = 6.7 \text{ nA}$ and $U_t = 0.6 \text{ V}$ for a LB film of **1** and $I_0 = 11.2 \text{ nA}$ and $U_t = 0.6 \text{ V}$ for a LB film of **2** yielded a tip-substrate distance estimation of 1.0 and 0.9 nm, in good agreement with the thicknesses of the LB films of **1** and **2**, respectively, allowing the STM tip to be positioned in contact with the top of the LB films for acquiring I - V curves. Fig. 3 shows all the I - V curves recorded (*ca.* 300 curves from different locations and various substrates) using these set-point parameters as well as the average curve for LB film of **1** (Fig. 3b) and **2** (Fig. 3c). The average I - V curves were

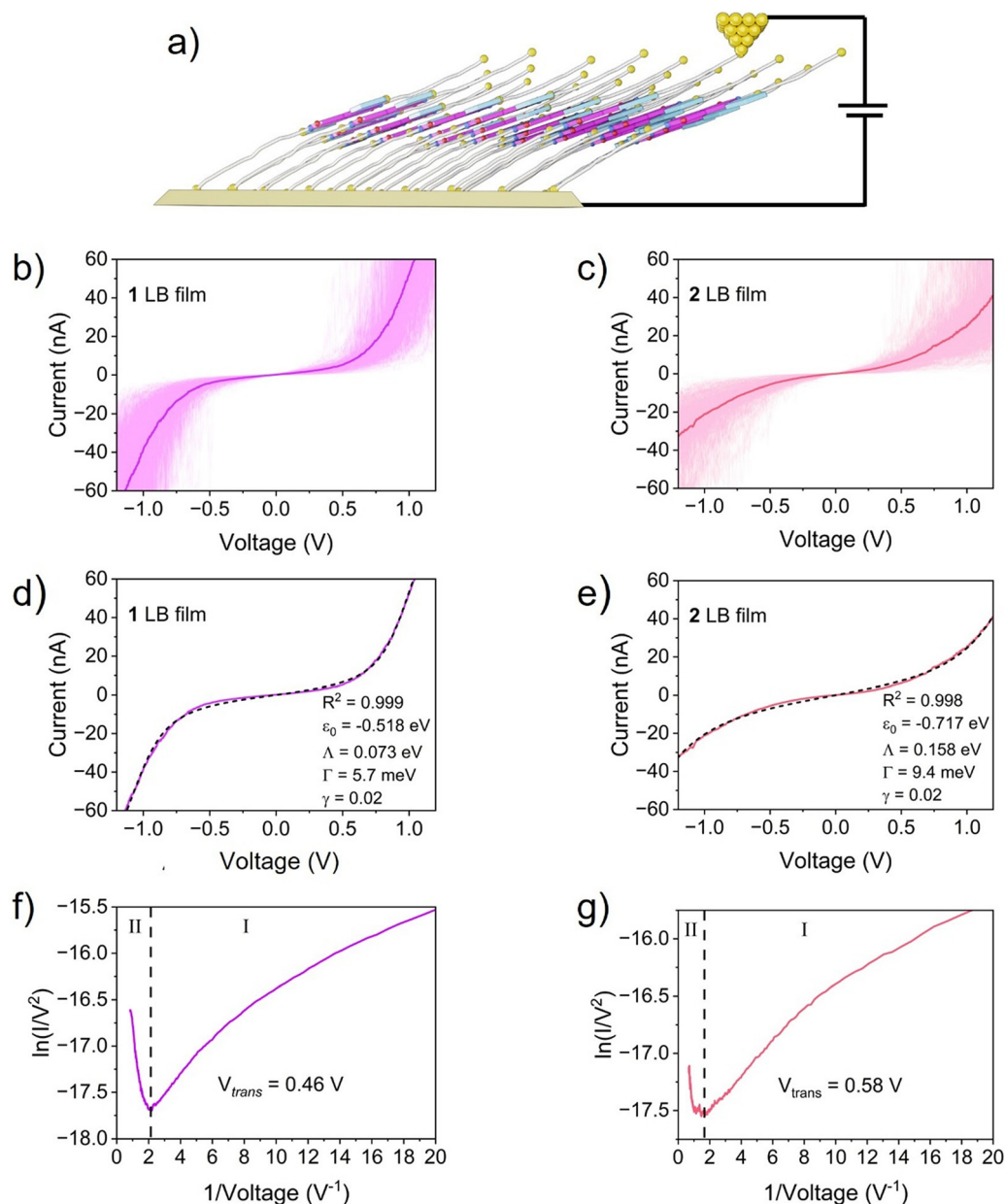


Fig. 3 (a) Cartoon showing the molecular arrangement within the LB films. Note that compound **1** showed a higher tilt angle and more gauche conformations than **2** as both compounds showed similar thicknesses even when **1** is 0.5 nm longer. *I*–*V* curves (ca. 300) recorded for (b) **1** LB film transferred at 7 mN m^{−1} using as set-point parameters *I*₀ = 6.7 nA and *U*_t = 0.6 V as well as the average one, (c) **2** LB film transferred at 12 mN m^{−1} using as set-point parameters *I*₀ = 11.2 nA and *U*_t = 0.6 V as well as the average one. (d and e) Best fit curves (black dashed lines) computed *via* eqn (2) for the average curves shown in (b) and (c). Key fit parameters are shown in the insets, along with the corresponding *R*² values. (f and g) Fowler–Nordheim plots for the average *I*–*V* curves of **1** and **2** LB film, respectively, where two distinct regimes (regions I and II) are evident.

nearly symmetric around zero and exhibited a characteristic sigmoidal behavior over the full bias voltage range (from −1.2 V to 1.2 V). In the low voltage region, from −0.3 V to 0.3 V, the curves were relatively linear (Ohmic regime), providing conductance values of 6.7 ± 0.2 nS ($8.7 \times 10^{-5} G_0$) and 7.8 ± 0.4 nS ($10.0 \times 10^{-5} G_0$) for LB films of **1** and **2**, respectively. The slight increase in conductance for LB films of **2** could be due to an effect of the tunneling barrier (lower thickness of this film) and molecular organization within the film. Nevertheless, the key point is that these conductance values were up to ca. 3.7 times

higher than those obtained from ‘conventional’ single-molecule junctions formed from low-coverage molecular films using the *I*(*s*) technique,⁴⁸ namely 1.8 ± 0.4 nS ($2.3 \times 10^{-5} G_0$) and 2.1 ± 0.3 nS ($2.7 \times 10^{-5} G_0$) for **1** and **2**, respectively (Fig. S12, Experimental section and SI for further details). To the best of our knowledge, this increase in conductance for the LB films of **1** and **2** respect to the respective single-molecule junctions has not been observed before. For example, OPE derivatives with different anchor groups assembled as LB films exhibit conductance values similar to or lower than those

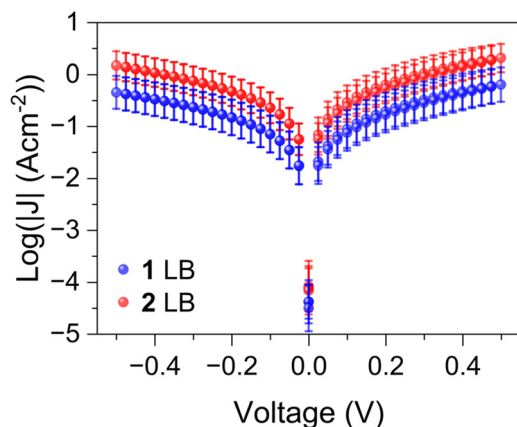


Fig. 4 Gaussian mean values of $\text{Log}(|J|)$ versus V for the EGaIn junctions formed for **1** (blue) and **2** (red) LB films. Error bars represent the standard deviation of each distribution.

obtained for single-molecule junctions using the $I(s)$ technique, despite the formation of H- or J-aggregates in the LB films.^{58–60,62,63} Therefore, this increase in the conductance was attributed to the existence of those intermolecular charge-transfer interactions between T-DPP moieties of neighboring molecules,^{54–56} as observed by UV-vis spectroscopy (Fig. 1c and d and Fig. S6). This was corroborated by using the $I(s)$ technique to determine the conductance of molecules assembled into a LB film of **1**^{49–52} (see Experimental section for further details). In this case, the junctions were formed by placing the atomically sharp gold STM tip at a given distance enough to penetrate the **1** LB film ($U_t = 0.6$ V and $I_0 = 10$ nA as set-point parameters). As the STM tip penetrates into the film, this measurement approach is inherently destructive to the monolayer structure, resulting in the disruption of intermolecular interactions. This occurs because the molecule (or molecules) initially trapped within the junction must tilt toward a more horizontal orientation to accommodate the vertical approach of the tip, subsequently, during the measurement, these molecules are

This trend in conductance is also consistent with the lower ΔE (HOMO–LUMO gap) estimated from the normalized UV-vis spectra.^{64,65} For a LB film of **1**, ΔE is 1.95 eV (nearly identical for a **2** LB film, 1.98 eV), whereas for **1** in solution it is 2.20–2.18 eV, regardless of solvent polarity (chloroform, ethanol or hexane, see Fig. S7). Additionally, these conductance values were higher than those obtained for LB films of oligo(phenylene–ethynylene) (OPE) derivatives,⁵⁹ despite the presence of two insulating alkyl chains in **1** and **2** (Fig. 1). All these results confirm the T-DPP moiety as an excellent candidate to be used as high conductance molecular core in the design of future large-area molecular electronic devices.

To estimate the influence of the intermolecular interactions on the conductance of the LB films, a recent theoretical framework based on off-resonance single level model (or SLM) was applied.⁶⁶ This approach allows the quantification of intermolecular interactions through the Λ parameter (the half-width at half-maximum of the molecular orbitals (MO) density of states (DOS)),⁶⁶ as the MO of a given molecule can experience an additional broadening (often referred as proximity broadening) due to interactions with surrounding molecules within the assembly. Therefore, Λ accounts not only for the MOs–electrode couplings (Γ), but also the additional broadening arising from intermolecular interactions. Using eqn (2), the average I – V curves for a LB film of **1** and **2** shown in Fig. 4b and c were fitted at room temperature using a five-thirds protocol⁶⁷ while fixing the number of molecules to $N = 1$ per junction. This assumption is justified because the ‘STM touch-to-contact’ method forms single-molecule junctions with individual molecules within substrate-supported monolayers, as demonstrated by using the $I(s)$ technique to determine the conductance of molecules assembled into a LB film of **1** (see Fig. S13). This fitting procedure allowed us to determine the optimal values of the free (unconstrained) model parameters Γ , Λ , ε_0 (the MO energy offset relative to electrodes’ Fermi energy), and γ (a dimensionless parameter that quantifies the bias dependence of the MO energy relative to the Fermi energy of the electrodes).

$$I = \frac{NG_0\Gamma^2}{e\Lambda} \left[\text{Im}\psi \left(\frac{1}{2} + \frac{\Lambda}{2\pi k_B T} + i \frac{\varepsilon_V + \frac{eV}{2}}{2\pi k_B T} \right) - \text{Im}\psi \left(\frac{1}{2} + \frac{\Lambda}{2\pi k_B T} + i \frac{\varepsilon_V - \frac{eV}{2}}{2\pi k_B T} \right) \right] \quad (2)$$

‘lifted’ until the molecule bridge(s) breaks. The good agreement between the conductance value obtained from ‘conventional’ single-molecule junctions of **1**, 1.8 ± 0.4 nS (Fig. S12) and that measured for the LB film of **1** (1.9 ± 0.45 nS), Fig. S13, using the $I(s)$ method in both cases, confirmed that the observed increase in the conductance arises from intermolecular charge-transfer interactions present in the LB film. Additionally, similar break-off distances were observed for a single-molecule junction of **1** (1.39 nm, Fig. S12e) and for a molecule assembled into a **1** LB film (1.37 nm, Fig. S13b). Both values are greater than the thickness of the LB film of **1** (1 nm, Fig. S9), corroborating that the molecule(s) is lifted during the measurement, inducing the rupture of these intermolecular charge-transfer interactions.

Fig. 3d and e demonstrate the excellent agreement between the experimental data and the fits to eqn (2) as well as the high coefficient of determination R^2 , with values close to unity. This confirms the validity of this theoretical framework for determining the model parameters, particularly Λ and Γ , and for assessing the impact of intermolecular interactions within the LB films on the conductance. The extracted values of Λ were 0.073 and 0.158 eV for a LB film of **1** and **2**, respectively, in agreement to those reported for SAMs of alkyl di(mono)thiols or oligophenylene di(mono)thiols.⁶⁶ Importantly, we found that $\Lambda \gg \Gamma$, providing clear evidence that the intermolecular interactions play a dominant role in the enhanced conductance of the LB films compared to the ‘conventional’ single-molecule

junctions formed from low-coverage molecular films using the $I(s)$ technique, where these intermolecular interactions does not exist. The lower value of A for a 1 LB film compared to 2 LB film is likely due to a higher proportion of gauche conformations in the longer alkyl chains present in **1** (Fig. 1a), which influence in the ability of molecules to organize themselves into monolayers. Therefore, these conformational differences may reduce intermolecular van der Waals (vdW) interactions between the alkyl chains in the LB film of **1** to favour charge-transfer from the thiophene units to the DPP moieties of neighboring molecules; thereby weakening intermolecular coupling.⁶⁶ It should be noted that the charge transport in these systems is primarily governed by the T-DPP core.

To obtain more information about the electrical properties of these LB films, a Fowler–Nordheim plot was constructed using eqn (3):

$$\ln\left(\frac{I}{V^2}\right) \propto \frac{-4d\sqrt{2m_e\phi^3}}{3\hbar q}\left(\frac{1}{V}\right) \quad (3)$$

where ϕ is the effective height of the tunneling barrier, d is the barrier width, m_e is the effective electron mass, and q is the elementary charge. As shown in Fig. 3f and g, $\ln(I/V^2)$ increases with $1/V$ in the low-bias region (region I), which was indicative of direct tunneling. Meanwhile, region II exhibited a negative slope, with $\ln(I/V^2)$ scaling linearly with $1/V$, which corresponds to field emission behavior. The transition point between these regions is known as the transition voltage, V_{trans} , which is linearly correlated with the energy difference between the frontier molecular orbitals and the metal Fermi level, although without being directly equal to it.⁶⁸ The obtained V_{trans} values, 0.46 and 0.58 for LB films of **1** and **2**, respectively, were lower than or comparable to those obtained for conjugated self-assembled molecular wires^{68–71} and notably lower to those obtained for alkanedithiol self-assembled monolayers (SAMs),^{68,72} suggesting again the merits of the T-DPP moiety as backbone in the design of large-area junctions. The lower V_{trans} observed for the LB film of **1** compared to **2** cannot be explained solely by the tunnelling length. Notably, the LB film of **1** exhibits a smaller tilt angle with respect to the substrate (27° vs. 32° for **2**), suggesting a higher proportion of gauche conformations in the longer alkyl chains. Although this results in comparable effective film thicknesses, it also suggests a lower degree of molecular order at the interface. Therefore, the observed conductance differences likely arise from a combination of tunnelling length, molecular packing, and interfacial electronic effects.^{73,74}

3.2.2. Eutectic gallium–indium (EGaIn) as a large-area top-contact electrode. As mentioned, the “STM touch-to-contact” method is suitable for the formation of single-molecule junctions from monolayer films for estimating the electrical properties of single molecules embedded in monolayers, which can be affected by intermolecular charge-transfer processes. In order to probe the electrical properties of these large-area LB films, *i.e.*, the charge transport across many molecules contacted simultaneously, large-area molecular junctions were prepared using a liquid metal eutectic gallium–indium (EGaIn) alloy as a

soft top-contact electrode. EGaIn is a low-viscosity liquid metal that exhibits high electrical and thermal conductivity at room temperature.^{75–80} Among its applications, EGaIn has been widely employed for the electrical characterization of self-assembled monolayers of a variety of organic molecules deposited on different substrates,^{81–83} thanks to its combination of liquid-like properties and solid-like mechanical stability. When exposed to air, the alloy spontaneously develops a thin GaOx ‘skin’ providing a stabilizing non-Newtonian behavior to the liquid metal, and allowing to form liquid cone-shaped tips suitable for junction formation, with reproducible contact geometries, while preventing metal penetration into the organic monolayer *via* van der Waals interactions with the SAM. This oxide acts as a self-limiting tunneling barrier, contributing minimally to the total junction resistance while ensuring mechanical protection of the molecular monolayer during junction formation.

Molecular junctions based on LB films of **1** and **2** were prepared as described in the Experimental section following a similar methodology reported in literature.^{79,84–86} Current density (J – V) curves were measured in the ± 0.5 V bias range for both LB films. Individual $\text{Log}|J|$ – V traces (Fig. S15) exhibited bias-symmetric V-shaped and non-rectifying behavior, with minimal hysteresis and excellent reproducibility across all samples. This symmetry around 0 V is consistent with tunneling as the dominant charge transport mechanism.^{86–89} The averaged $\text{Log}|J|$ curves (red curves in Fig. S15) were obtained through Gaussian distribution analysis at each bias value, further confirming the uniformity of the electrical response. All the measured junctions demonstrated an excellent monolayer integrity and stable junction formation. LB films of **2** particularly exhibited a slightly narrower dispersion and higher average current densities, consistent with more efficient electron tunneling through a thinner barrier.

Furthermore, the reproducibility and yield of junction formation were evaluated. The yield was defined as the percentage of successful J – V traces measured from working junctions relative to the total number of recorded traces including short-circuited ones. A total of 13 junctions were measured for LB films of **1** and 12 for LB films of **2**, with 10 J – V scans recorded per junction (Tables S1 and S2). The overall yield of the working junctions was therefore 80.0% for LB films of **1** and 81.3% for LB films of **2**. These high yields reflected the intrinsic quality and robustness of the molecular junctions reported here.

Fig. 4 shows a comparative plot of the Gaussian means of $\text{Log}|J|$ as a function of applied bias. Tunneling currents measured for **1** LB film were slightly lower than those of **2** LB film, reflecting the expected exponential dependence of tunneling current on molecular length.^{84,85,89,90} Although the difference is small and falls within the experimental standard deviations, this trend was consistently observed, suggesting a subtle but real effect of tunneling barrier and molecular organization within the film, in agreement with that observed using the ‘STM touch-to-contact’ method.

To statistically examine the current density variability, histograms of $\text{Log}|J|$ values at +0.5 V and –0.5 V for each type of

monolayer, including all the samples investigated, were analyzed (Fig. S16). The values of $\text{Log}[I]$ appear to be normally distributed and characterized by sharp average peaks. Thus, the histograms were fitted with normal (Gaussian) distributions, from which we extracted the mean values and associated standard deviations. Notably, both LB films exhibited unimodal distributions at both applied biases. For LB films of **1**, the distributions peak at -0.22 ± 0.47 and -0.36 ± 0.46 at $+0.5$ V and -0.5 V, respectively. In contrast, LB films of **2** display main peaks at 0.30 ± 0.36 and 0.18 ± 0.36 at $+0.5$ V and -0.5 V, respectively. The smaller standard deviations for LB films of **2** indicate a less dispersed junction population and reduced conductance variability compared with LB films of **1**, consistent with the lower dispersion observed in the $\text{Log}[I]$ -V measurements (Fig. S15). These results confirm that both LB films enabled reproducible bias-symmetric tunneling transport curves measured in large-area metal/monolayer//GaOx/EGaIn junctions. This behavior mirrors that observed with the 'STM touch-to-contact' method, revealing a consistent physical picture across both small- and large-area junction architectures.

4. Conclusions

In this study, two DPP derivatives bearing alkyl chain of different lengths at both termini ($(\text{CH}_2)_n$ with $n = 4$ or 6) were synthesized and assembled into well-packed Langmuir-Blodgett films. A combination of surface pressure and surface potential *vs.* area per molecule isotherms, Brewster angle microscopy and reflection spectra was used to characterize the films at the air-water interface. These measurements confirm the formation of true monomolecular films for both compounds and provide evidence for intermolecular charge-transfer interactions between the thiophene-DPP moieties of neighboring molecules. Atomic force microscopy measurements showed homogeneous films, which could be transferred largely undisturbed onto solid substrates. Electrical characterization using the 'STM touch-to-contact' method revealed a subtle dependence on conductance on molecular length and, more notably, a pronounced enhancement in conductance (*ca.* 3.7-fold) compared to 'conventional' single-molecule junctions formed from low-coverage molecular films using the $I(s)$ technique. This increase in conductance was attributed to intermolecular charge-transfer interactions within the ordered LB assemblies. Additionally, transition voltages (V_{trans}) determined for both LB films are significantly lower than, or comparable to, those reported for conjugated self-assembled molecular wires and, markedly lower than those of alkane-dithiol self-assembled monolayers. Large-area molecular junctions fabricated using eutectic gallium-indium as a soft top-contact electrode exhibited high junction yields and charge transport characteristics consistent with the 'STM touch-to-contact' method measurements, establishing a unified transport picture across both small- and large-area junctions. Together, these results highlight the intrinsic quality and robustness of LB-based molecular junctions and underscore

the DPP moiety as an excellent backbone for the development of future molecular electronic devices.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

All raw and processed data generated in this study are available from the corresponding author upon reasonable request.

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary information (SI). Supplementary information: Atomic force microscopy, Brewster angle microscopy, UV-visible spectra, quartz crystal microbalance measurements, XPS spectra, single molecule conductance and eutectic gallium-indium measurements are included in SI. See DOI: <https://doi.org/10.1039/d6tc01216g>.

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