



## Mapping frontier molecular orbitals using photocurrents

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In the regime of coherent transport, the conductance of a molecular junction is governed (Fig. 1a) by the probability of electron transmission between the metal electrodes, a physical property which is affected significantly by the hybridization of frontier molecular orbitals (FMOs) with the continuous band of energy levels on the electrodes. The extent of hybridization is determined primarily by two factors [1], i.e., (i) the energetic alignment ( $\Delta E$ ) of the molecular orbital with respect to the metal Fermi level and (ii) the broadening ( $\Gamma$ ) of the molecular orbital on account of hybridization. Unlike the conventional regime of electron transport, when a pulsed laser is applied to a molecular junction, resonant transport may occur (Fig. 1b) because photoinduced electrons travel through the lowest unoccupied molecular orbital (LUMO) + 1 and LUMO + 2 orbitals of the molecule bridging the two electrodes, resulting in enhanced photocurrents. Furthermore, if a bias voltage is applied to the molecule, it may cause a shift in the energy alignment of the molecular orbitals. In order to achieve resonant transport under bias condition, it is necessary to adjust the energy of the pulsed laser in order to reach the energy levels which have undergone shift (Fig. 1c). A thorough understanding of the distribution of FMOs at the molecule/electrode interface is crucial for our understanding of electron transport in molecular junctions.

Notable advances have been made in recent years in the visualization of the energy level alignment of molecular FMOs with respect to electrodes in single-molecule junctions. These techniques encompass transition voltage spectroscopy [2], thermopower measurements [3], and gating technique [4,5]. Traditional electrical characterization techniques, however, are hindered by localized thermal effects and are unable to provide a quantitative characterization of interfacial energy alignment across a broad energy range, particularly beyond the highest occupied molecular orbital (HOMO)-LUMO energy range. As a result, achieving energy-resolved measurements of energy alignment at the interface has emerged as a critical technical challenge in the field of molecular electronics.

In a recent article published in *Nature Materials*, Hong and co-workers [6] have introduced a ground-breaking approach to overcome the limitations of conventional electrical characterization techniques. They propose using ultrafast laser pulses of extremely short duration with weak coupling to the atomic lattice to effectively avoid the accumulation of localized thermal effects. This protocol provides an unprecedented opportunity to investigate and understand complex energy relationships at the

interfaces between molecules and electrodes in single-molecule junctions. Furthermore, it enables the manipulation of photoelectron tunneling processes by leveraging the unique electronic structure of individual molecules and proves the generality of the protocol.

In their investigation, the team developed (Fig. 1d) a home-made scientific instrument in which efficient conductance and photocurrent measurements could be realized simultaneously in single-molecule junctions based on the scanning tunneling microscope-based break junction (STM-BJ) technique. The detection of transient photocurrents using this technique involves four steps. Firstly, the construction of the single-molecule junction is confirmed by using the conductance signal as feedback. Secondly, once the molecular junction is formed, the positions of the two electrodes are fixed and suspended for 200 ms. Thirdly, during this 200-ms period, the relay is switched to the photodetection circuit, and the photocurrent signal of the single-molecule junction is recorded using a lock-in detection technique. Lastly, when the suspension time is over or the molecular junction breaks on account of thermal fluctuations or mechanical perturbations, the real-time conductance decreases rapidly. A new cycle detection of the conductance and photocurrent begins employing a negative feedback system circuit.

The relationship between photocurrent and the laser pulse energy was investigated (Fig. 1d, inset) with diketopyrrolopyrrole (DPP) as a model compound. The results reveal (Fig. 1e) two distinct peaks located at approximately 1.45 and 1.70 eV. These two peaks can be attributed (Fig. 1b) to the resonant transport of photoinduced electrons through two different FMOs. In order to validate this hypothesis, density functional theory calculations were carried out to determine the transmission spectrum of the DPP single-molecule junction. The results reveal (Fig. 1f) that the FMOs based on DPP—namely LUMO + 1 and LUMO + 2—are located at energy positions of 1.25 and 1.72 eV, respectively, with respect to the calculated electrode Fermi level. After adjusting the energy positions of LUMO + 1 and LUMO + 2 obtained from the calculations, the corrected energy levels are 1.58 and 2.05 eV, respectively. These values align with the results of the experimental interfacial energy alignment model, indicating a good agreement between theoretical and experimental results. In addition, the researchers have demonstrated the feasibility of bias-voltage gating by applying a bias voltage from 0.2 to 0.5 V to the substrate, resulting in a collective shift of molecular energy alignment

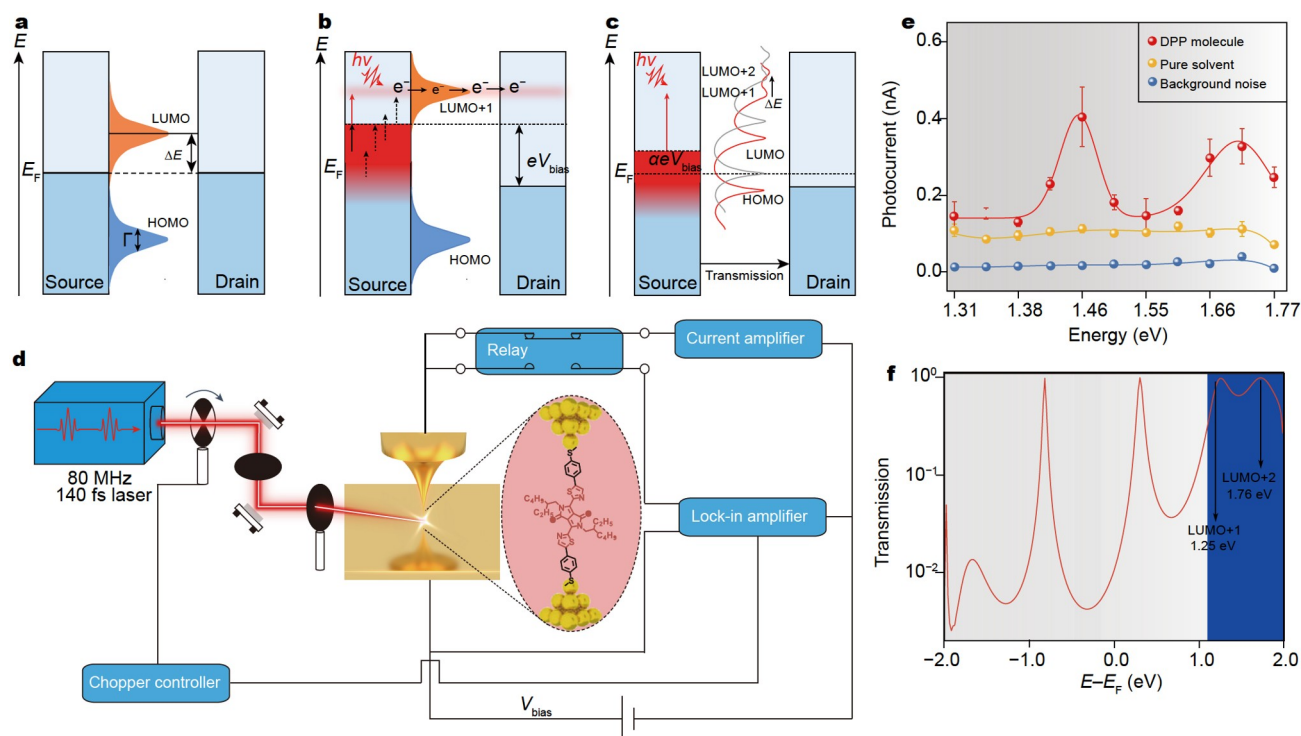
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**Figure 1** (a–c) Schematic illustrations showing charge transport processes of three different single-molecule junctions, i.e., (a) electron tunneling under zero bias, (b) laser-driven photoelectron tunneling through FMOs, and (c) electric-field-induced energy shift of FMOs based on laser-driven photoelectron tunneling. (d) Schematic of the single-molecule photoelectron tunnelling spectroscopy set-up. (e) Energy-dependent photocurrent of the DPP molecule. (f) Calculated transmission spectrum of the DPP molecule. Reprinted with permission from Ref. [6]. Copyright 2023, Nature Publishing Group.

(Fig. 1c). The mapped transmission spectra also exhibit a simultaneous parallel shift, providing solid evidence for the feasibility of this bias voltage gating approach.

The technique presented in this research represents a milestone in the field of molecular electronics, enabling the valuable and comprehensive characterization of the energy level alignment between the molecule and the metal electrodes. Utilizing the advantages of femtosecond wavelength tunability and avoiding the thermal effects of the tip electrode, the energy distribution with an energy window above 1.5 eV can be mapped out by detecting photocurrent through the single-molecule junction. The sensitivity of photocurrent response also enables its application in investigating the luminescence mechanism and lifetime of optoelectronic devices on the single-molecule scale. Additionally, the external electric field, which can be used for gating the FMOs of molecular junctions in parallel by an energy change of  $\Delta E$ , provides a feasible experimental solution for investigating the dynamics and mechanisms of single-molecule scale electric-field-catalyzed reactions in the future [7].

Since the pulsed light used in the reported technique is in the near-infrared range, the corresponding energy in this range is still relatively low and should be able to map to the LUMO orbital. However, the results presented in this article fail to map to the LUMO orbital. The question arises—is it possible to

extend the pulse light range to longer wavelengths in order to achieve the mapping of lower energy orbitals in molecules? Nevertheless, this breakthrough sets the stage for further advances in designing responsive optoelectronic devices and investigating the ultrafast dynamics based on single-molecule devices.

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