

## Photoconductance from Exciton Binding in Molecular Junctions

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### S Supporting Information

**ABSTRACT:** We report on a theoretical analysis and experimental verification of a mechanism for photoconductance, the change in conductance upon illumination, in symmetric single-molecule junctions. We demonstrate that photoconductance at resonant illumination arises due to the Coulomb interaction between the electrons and holes in the molecular bridge, so-called exciton-binding. Using a scanning tunneling microscopy break junction technique, we measure the conductance histograms of perylene tetracarboxylic diimide (PTCDI) molecules attached to Au-electrodes, in the dark and under illumination, and show a significant and reversible change in conductance, as expected from the theory. Finally, we show how our description of the photoconductance leads to a simple design principle for enhancing the performance of molecular switches.

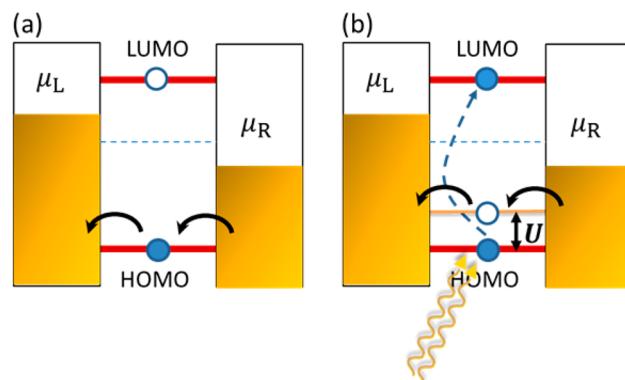
The field of molecular electronics is driven by the objective of designing molecular devices that perform a specific electronic function, either mimicking current technologies<sup>1–4</sup> or providing new features that are unavailable with traditional semiconductor devices.<sup>2,5</sup> A major direction in this field is that of “Molecular Optoelectronics”, namely, the control over electronic properties of the molecular junctions by optical means.<sup>2,6–8</sup> Specifically, we focus here on the property of photoconductance (PC), namely, a change in the electronic conductance under illumination, which may be used for, e.g., optoelectronic switching.<sup>2,6,9,10</sup>

To date, there are several recognized mechanisms for PC. The first mechanism is a photoinduced structural change.<sup>11–17</sup> The second is the opening of additional conduction channels under illumination, resulting from an inherent asymmetry in the junction, following resonant optical transitions.<sup>6,18,19</sup> The large degree of molecular asymmetry, required by this mechanism to generate a molecular structure with some similarity to a semiconducting donor–acceptor system, is reflected in the choice of molecular moiety for single-molecule optoelectronic systems.<sup>20–22</sup> A third mechanism is the opening of photoinduced conduction side-bands in the single-electron transmission function, so-called adiabatic photoassisted tunneling (or Tien–Gordon mechanism).<sup>4,6,10,23–27</sup>

Here we propose a mechanism for molecular PC, based on the formation of bound excitons in the molecule. We demonstrate theoretically that such exciton formation can lead to photoconductivity even in molecules that are perfectly symmetric and

without any structural changes. The theory is followed by experimental demonstration of PC in a single-molecule junction with a symmetric molecular moiety, perylene tetracarboxylic diimide (PTCDI), showing clear difference in the conductance histograms under illumination and in the dark. Our model provides a simple design principle relating the molecular electronic structure and the photoconductance on/off ratio, demonstrating that with an optimal choice of the molecular system the on/off ratio can be larger than 10<sup>5</sup>.

Let us start with a brief outline of the origin of PC in symmetric molecules. Consider the simplest model for transport through a molecular junction,<sup>4</sup> namely, the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, which we shorthand here as *H* and *L* for convenience) coupled to electrodes, as illustrated in Figure 1. Assume that the electrodes’



**Figure 1.** Schematic presentation of transport through a molecular junction, comprising two electrodes held at a voltage difference and a molecular with two frontier orbitals. (a) In the dark, the current is dominated by hole-transport through the HOMO. (b) Under illumination, the LUMO becomes partially filled. Consequently, a hole entering the HOMO is attracted to it, resulting in an effective shift of the HOMO level toward the Fermi level and an increase in conductance.

Fermi level is closer to the *H* than the *L*, in which case the conductance is dominated by tunneling of holes to the *H* (similar arguments will hold also for *L*-dominated transport).

In the dark, the conductance depends (exponentially) on the energy difference between the *H* and the electrodes’ Fermi level. Under illumination (where the frequency is in or close to resonance with the *H*–*L* gap), electrons from the *H* are excited to

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the  $L$ , which is now partially filled. A hole that tunnels from the electrode to the  $H$  now feels the charge in the  $L$  and is attracted to it. As a result, the  $H$  energy is pushed toward the Fermi level, resulting in an increase in conductance.

Consider the generic model for a molecular junction consisting of a molecule between two metallic electrodes.<sup>4,28,29</sup> We take into account only the  $H$  and  $L$  molecular orbitals, and since electron spin plays no part in the PC, we consider spinless Fermions (see discussion in SI). The corresponding Hamiltonian of the system (in the dark) is

$$\mathcal{H}_0 = \mathcal{H}_M + \mathcal{H}_{L,R-M}$$

$$\begin{aligned} \mathcal{H}_M &= \sum_{n=H,L} \epsilon_n d_n^+ d_n + U \hat{n}_H \hat{n}_L \\ \mathcal{H}_{L,R-M} &= \sum_{k \in \{L,R\}} \epsilon_k c_k^+ c_k + \sum_{k \in \{L,R\}} (V_k c_k^+ d + h.c.) \end{aligned} \quad (1)$$

where  $c_k$  ( $c_k^+$ ) are annihilation (creation) operators for electrons in the electrodes (with energy  $\epsilon_k$ ),  $d_n$  ( $d_n^+$ ) are annihilation (creation) operators for electrons in a molecular level  $|n\rangle$  with energy  $\epsilon_n$ , where  $n = H, L$  marks the HOMO and LUMO level,  $\hat{n}_n = d_n^+ d_n$  is the number operator, and  $U$  is the Coulomb term, which represents the electrostatic repulsion between electrons in the molecule. Alternatively,  $-U$  can be considered as the molecular exciton binding energy and represents the difference between the optical gap and the fundamental (or transport) gap (in the presence of metallic electrodes).<sup>30–32</sup>

Under illumination, additional terms should be added to the Hamiltonian, describing the impinging photons and their interaction with electrons<sup>6,33</sup>

$$\mathcal{H}_{ph} = \hbar \omega a^+ a + \lambda (a^+ d_H^+ d_L + a d_L^+ d_H) \quad (2)$$

where  $a^+(a)$  creates (annihilates) a photon with energy  $\hbar \omega$ . The second term describes an excitation of an electron from the  $H$  to the  $L$  by photon absorption (and the reverse process), with  $\lambda$  as the electron–photon interaction, which in turn depends on the molecular dipole moment.

At resonance (i.e., when  $\hbar \omega \simeq E_{\text{LUMO}} - E_{\text{HOMO}}$ ) and under weak molecule-electrode coupling, the conductance through the junction can be evaluated using the rate equation method<sup>34,35</sup> (see SI for further details). The resulting conductance depends on a small set of relevant parameters: orbital energies of the HOMO and LUMO,  $\epsilon_H$  and  $\epsilon_L$ , respectively, the electrode chemical potential  $\mu$ , exciton binding energy  $U$ , transfer rates from the HOMO and LUMO to the left (right) electrodes,  $\gamma_{H,l}$  ( $\gamma_{H,r}$ ) and  $\gamma_{L,l}$  ( $\gamma_{L,r}$ ), respectively, and ambient temperature  $T$ . The effect of illumination is encoded through a single parameter,  $v$ , which is the effective rate of excitation of electrons from the  $H$  to the  $L$  (note that  $v$  is an effective rate, which includes the molecular absorption cross section, the rate of impinging photons and the exciton lifetime, see SI). The parameters and their numerical values used in the calculation are described in Table 1.

We are interested in the role of binding energy as the origin of PC in symmetric junctions. To see this effect, we first consider the case of  $U = 0$ . Although the full expression for the conductance is too cumbersome to be presented here, insight can be gained by studying different limiting cases. For simplicity, we assume  $\gamma_{H,l} = \gamma_{L,l} = \gamma$ ;  $\gamma_{H,r} = \gamma_{L,r} = \tilde{\gamma}$ , i.e., the symmetry is broken between left and right electrodes. Under weak illumination, the expression for the conductance becomes linear in  $v$ .

**Table 1. Description and Numerical Values of Parameters**

parameter	$\epsilon_H$	$\epsilon_L$	$\mu$	$\gamma$
description	HOMO level <sup>a</sup>	LUMO level <sup>a</sup>	chemical potential <sup>a</sup>	molecule-electrode electron transfer rate <sup>a</sup>
values	-6.31 eV	-3.8 eV	-5.3 eV	$\sim 60 \text{ ns}^{-1}$
parameter	$T$		$U$	$v$
description	temperature <sup>a</sup>		exciton binding energy <sup>b</sup>	HOMO–LUMO effective excitation rate <sup>b</sup>
values	300 K		0.2 eV	$\sim 0.02 \text{ ns}^{-1}$

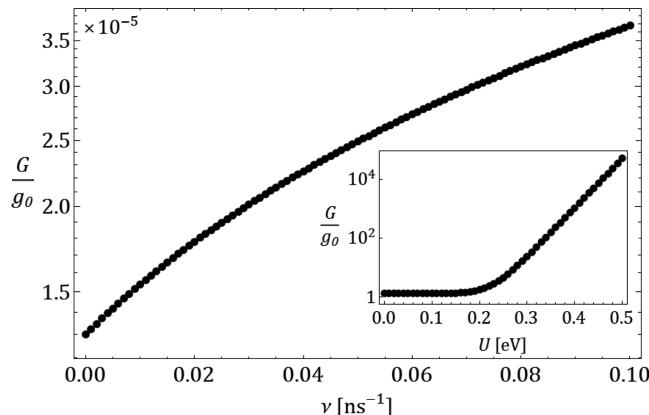
<sup>a</sup>Evaluated from the gas phase (see SI). <sup>b</sup>Evaluated from fit to experiments (Figures 3 and 4).

$$G \approx G^{(0)} + G^{(1)}v$$

$$G^{(1)} = [f(\epsilon_H) + 2(f(\epsilon_H) - 1)] \frac{\partial f}{\partial \epsilon} \Big|_{\epsilon_L} \left( \frac{1}{2} \frac{\gamma - \tilde{\gamma}}{\gamma + \tilde{\gamma}} \right)^2 \quad (3)$$

where  $G^{(0)}$  is the conductance in the dark and  $f(\epsilon)$  is the Fermi–Dirac distribution function (see SI). One can immediately see that if  $\gamma = \tilde{\gamma}$ , i.e., if the molecular junction is symmetric, the conductance is independent of  $v$ . This means that there is no difference between the conductance at  $v = 0$  (in the dark) and  $v \neq 0$  (under illumination), and consequently, no PC effect can be observed<sup>33</sup> (these conclusions hold also for the full expression of  $G$ , which is a complicated function of  $v$ ).

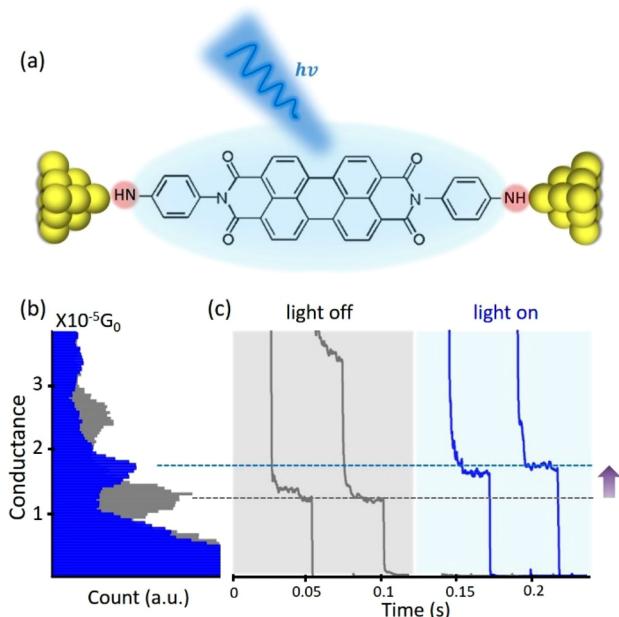
However, if  $U \neq 0$ , the exciton-binding mechanism comes into play, and PC will be observed even with the full symmetry preserved. In Figure 2, we plot the conductance (in units of the



**Figure 2.** Conductance (in units of the conductance quantum) as a function of the photoinduced HOMO–LUMO excitation rate  $v$ , for a symmetric molecular junction with finite Exciton binding energy  $U$  (see text for numerical values). Inset: Conductance at a finite  $v$  as a function of the exciton binding energy  $U$ , demonstrating an exponential increase in photoconductance as  $U$  becomes comparable to the HOMO–Fermi level energy difference.

quantum conductance  $g_0 = \frac{2e^2}{h} \approx 7.75 \times 10^{-5} \text{ S}$ ) as a function of the illumination-induced  $H$ – $L$  transition rate  $v$  (see Table 1 for parameters, which were taken from comparison to experiment, see Figure 3 below). The conductance under illumination shows an increase with  $v$ , i.e., the onset of PC.

The inset of Figure 2 shows the conductance as a function of exciton binding energy for constant  $v = 0.02 \text{ ns}^{-1}$ , demonstrating that, above some threshold, the conductance under illumination grows exponentially with the exciton binding energy. The origin



**Figure 3.** (a) Schematic illustration of the experimental setup, a  $\text{NH}_2\text{-PTCDI-NH}_2$  molecule trapped in an STM-BJ setup and illuminated with laser light. (b) Conductance histograms in the dark (gray) and under illumination (blue). (c) Example for the conductance traces used to generate the histograms (see SI for further details).

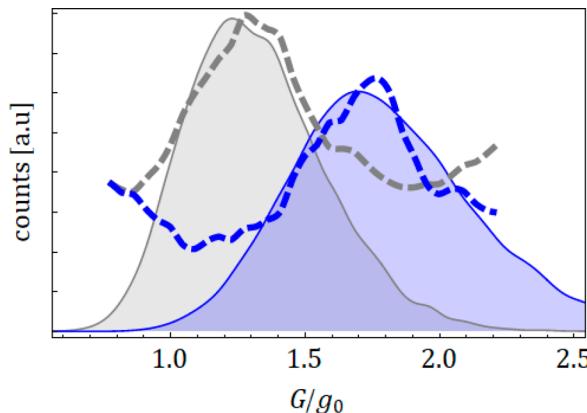
of this exponential dependence is the fact that conductance in general depends exponentially on the HOMO–Fermi level energy difference. This implies a design principle for high-performance molecular photoswitches: the optimal situation is such that the exciton binding energy is as large as the HOMO–Fermi level energy difference. Unfortunately, this poses two problems: (i) it is typically hard to calculate the binding energy since it is strongly affected by the presence of electrodes and can be very different in the molecular junction than in the gas-phase molecule,<sup>30–32</sup> and (ii) typically, one expects that increasing the exciton binding energy goes together with lowering of the  $H$  level. Nevertheless, this design principle can serve as a guide for future experiments.

To test the theory afore-described, our photoconductance single-molecule experiments were performed on scanning tunneling microscopy break junctions<sup>3,5,36–38</sup> (STM-BJs) with perylene tetracarboxylic diimide (PTCDI) molecules attached to Au-electrode via Au–amine bonds (Au–NH<sub>2</sub>–PTCDI–NH<sub>2</sub>–Au), depicted in Figure 3a. PTCDI and its derivatives are known to be highly photoactive, and have been extensively studied in recent years, leading to the fabrication of high-performance optoelectronic devices such as organic light-emitting diodes, solar cells, and photodetectors.<sup>39–43</sup> We used a monochromator (TLS 25 with spectral range 360 nm to 1000 nm) to apply photon emissions at fixed 495 nm wavelength (corresponding to an energy of 2.5 eV, in resonance with PTCDI's  $H$ – $L$  gap<sup>44</sup>), through an ultrathin ( $\sim 600 \mu\text{m}$  in diameter) fiber optical cable to the single molecular STM-BJs formed in toluene solution while monitoring the electronic current of the junction. Full experimental details are provided in the SI. Figure 3b shows conductance traces as the break junction is pulled, demonstrating the single-molecule nature of the transport measurements. Gray (blue) curves are measurements performed in the dark (under illumination). The conductance histogram after taking over 1000 conductance traces is shown in Figure 3c, demonstrating a clear

PC effect. The conductances in the dark are centered around  $G_{\text{dark}} \approx 1.25 \times 10^{-5} g_0$ , while the conductances under illumination are centered around  $G_{\text{light}} \approx 1.75 \times 10^{-5} g_0$ , yielding a PC on/off ratio of  $\sim 40\%$ , which is small yet statistically significant. Note that this on/off ratio is larger than the photoconductance recently reported in IR-illuminated single-molecule<sup>26</sup> and was obtained with visible light illumination, which may be advantageous for future applications. The conductance switching was perfectly reversible (i.e., upon switching off the illumination the conductance histogram regained its previous form), thus eliminating any possible structural changes in the junction.

The data of Figure 3 was used to evaluate the parameters in Table 1. The energies were calculated using Gaussian03 (see details in the SI) and are comparable to values found in the literature.<sup>44</sup> The molecule-electrode transfer rates  $\gamma$  were found by fitting the theoretical conductance with  $G_{\text{dark}}$  and the  $H$ – $L$  transfer rate  $v$  from fitting to  $G_{\text{light}}$ .

Since the experimental data is statistical, further information about the molecular junction can be extracted by studying the full histogram.<sup>45</sup> In Figure 4 we plot the experimental histogram



**Figure 4.** Conductance histograms (with subtracted background) for junctions in the dark (gray) and under illumination (blue). Dashed lines are the experimental data, and filled curves are theoretical calculations (see text for details).

(dashed lines) after extracting the tunneling background.<sup>4</sup> The filled solid lines are theoretical evaluations of the conductance in the dark (blue) and under illumination (gray), while allowing the  $H$  and  $L$  levels to fluctuate (assuming Gaussian fluctuations around the fitted values of Table 1 with variation width  $\delta E$ ).<sup>46,47</sup> We find that, due to the exponential dependence of the conductance on energy levels in off-resonance conduction,<sup>4</sup> a rather small amount of fluctuation,  $\delta E \approx 5 \text{ mV}$ , is required to fit the experimental histograms. If one assumes that it is the electron-molecule couplings that are fluctuating, then a variation of  $\frac{\delta \gamma}{\gamma} \approx 20\%$  in the molecule electrode couplings is required to fit the experimental histogram (not shown). Such a variation is rather small and not enough to reproduce an asymmetry required to give the measured photoconductance (see SI), thus corroborating the observation that the junctions are symmetric.

In summary, we have presented a combined theoretical–experimental study of photoconductance in symmetric single-molecule junctions. The change in conductance upon illumination (in the absence of built-in asymmetry) was linked to the formation of a bound exciton in the molecule, which in turn causes a shift in the local energy of the frontier orbitals. This implies that if a molecular junction with exciton binding energy similar in

magnitude to the HOMO–Fermi level energy difference can be found, it will serve a photoswitch with an on–off switch of several orders of magnitude. Further studies are required to test our hypothesis, including additional measurements with PTCDI derivatives and other symmetric light-absorbing molecules, illuminating with different wavelengths, and changing various junction parameters (molecule–electrode coupling via stretching<sup>3,48</sup> or changing the molecular orbitals using gating<sup>3</sup>).

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.7b10479](https://doi.org/10.1021/jacs.7b10479).

Further details on the theoretical calculation, further discussion on the role of asymmetry, and experimental details ([PDF](#))

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### Notes

The authors declare no competing financial interest.

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