

Resonant Photoconductance of Molecular Junctions Formed in Gold Nanoparticle Arrays

Markus A. Mangold,[†] Michel Calame,[‡] Marcel Mayor,[¶] and Alexander W. Holleitner^{*†}

[†]Walter Schottky Institut and Physik-Department, Technische Universität München, Am Coulombwall 4a, 85748 Garching, Germany

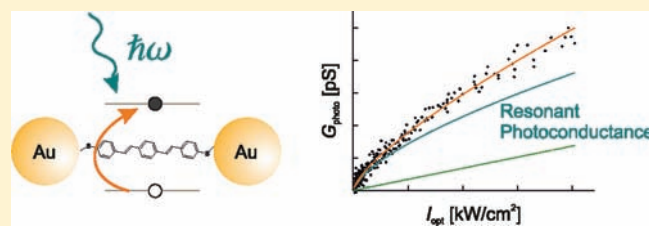
[‡]Departement Physik, Universität Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland

[¶]Departement Chemie, Universität Basel, St. Johannis-Ring 19, 4056 Basel, Switzerland

 Supporting Information

ABSTRACT: We investigate the photoconductance properties of oligo(phenylene vinylene) (OPV) molecules in metal–molecule–metal junctions. The molecules are electrically contacted in a two-dimensional array of gold nanoparticles. The nanoparticles in such an array are separated by only few nanometers. This allows to bridge the distance between the nanoparticles with molecules considered as molecular wires such as OPV. We report on the photoconductance of electrically contacted OPV upon resonant optical excitation of the molecules.

This resonant photoconductance is sublinear in laser intensity, which suggests that trap state dynamics of the optically excited charge carriers dominate the optoelectronic response.



INTRODUCTION

Since the proposal of a molecular rectifier by A. Aviram and M. A. Ratner,¹ a steadily increasing amount of research activity is dedicated to the introduction of molecules into electronic circuits.² A great variety of experimental techniques such as mechanically controllable break junctions, self-assembled monolayers on mercury droplets, crossed-wire tunnel junctions, and scanning probe microscopy have been developed in order to form stable electrical contacts to organic molecules.³ Characterization methods such as photoelectron spectroscopy, inelastic tunneling spectroscopy, and electrochemical gating have been successfully applied to understand the basic transport mechanism in metal–molecule–metal junctions.⁴ In addition, there have been several attempts to resolve the photocurrent signal of single molecules in molecular junctions.⁵ Theory predicts a large effect on the conductance of a molecular junction upon resonant as well as nonresonant optical excitation.⁶ However, the molecular photoconductance is typically overlaid by bolometric or plasmonic effects induced in the metallic electrodes of the molecular junctions.⁵

A promising approach to photocurrent spectroscopy of organic molecules contacted to metal electrodes consists in the use of metal nanoparticles as nanoscopic electrodes to the molecules. It was shown that organic molecules incorporated in nanoparticle arrays can interlink adjacent particles and form symmetric metal–molecule–metal junctions.⁷ The advantage of such a configuration is that the molecules can easily be accessed by optical means. It was shown that diarylethene molecules contacted in gold nanoparticle arrays maintain their optical switching activity when they are incorporated into a nanoparticle array.⁸ Further photoconductance observations in nanoparticle arrays were ascribed to

a bolometric conductance enhancement,⁹ to a plasmonic field enhancement,¹⁰ and to trap state filling in the nanoparticle cores.¹¹

Here, we report on the photoconductance of oligo(phenylene vinylene) (OPV) incorporated in gold nanoparticle arrays. We find a pronounced photoconductance arising upon resonant excitation of the OPV molecules. We determine the typical response time and the irradiation intensity dependence of this resonant photoconductance. Our results suggest that the charge carriers, which are resonantly excited in the OPV molecules, directly contribute to the current flow through the nanoparticle arrays. We can consistently model the dynamics of the resonant photoconductance by considering the filling and recombination of trap states in the nanoparticle arrays. Our results verify that individual molecules in metal–molecule–metal junctions can be functional modules of optoelectronic devices.

METHODS

Array Preparation. The gold nanoparticles were prepared by reduction of Au(III) as previously described.¹² Twenty milliliters of a heated reducing solution (0.2% (by weight) citric acid trisodium salt, 0.004% (by weight) tannic acid) was added to 80 mL of a boiling solution of 1% (by weight) HAuCl₄; the mixture was boiled under stirring for 10 min, then cooled down to room temperature. This resulted in Cl[−] stabilized gold particles with a mean diameter of 9.5 nm, as was confirmed by X-ray scattering.¹³

Formation of the nanoparticle array followed a protocol proposed by Huang et al.¹⁴ Ten milliliters of the Au nanoparticle solution was centrifuged for 60 min at 14 krpm and the supernatant water was removed. The

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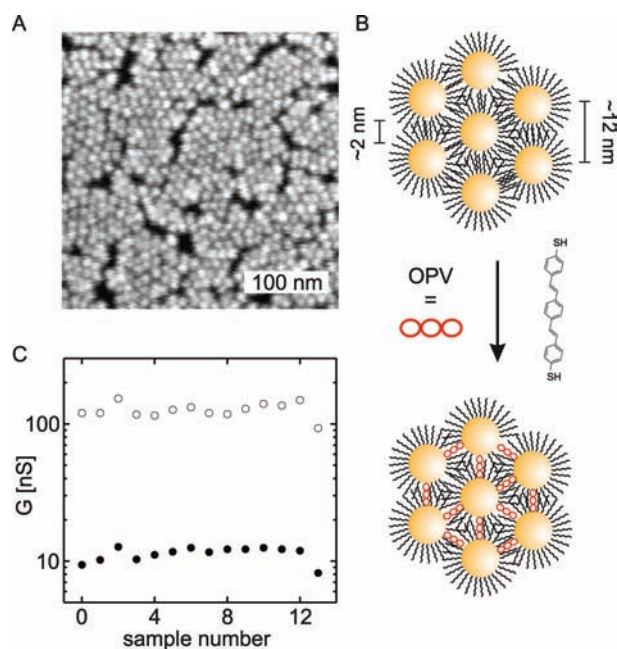


Figure 1. Nanoparticle array structure and conductance. (A) A scanning electron microscope (SEM) image of a nanoparticle array made from octanethiol coated gold nanoparticles; (B) sketch of the structure of a nanoparticle array and how the nanoparticles are interlinked by the OPV molecules during the molecular exchange; (C) the conductance of 14 individual nanoparticle arrays before (full circles) and after (open circles) the molecular exchange is plotted.

sedimented nanoparticles were dissolved in 10 mL of ethanol and 4 mL of a 2.4% (by volume) solution of freshly distilled octanethiol in ethanol was added. The octanethiols were bound to the gold particles overnight and the alkane coated particles were precipitated. The supernatant ethanol was removed the next day and the sediment was washed in fresh ethanol. After anew precipitation, the ethanol was removed and the nanoparticles were dissolved in 3.5 mL of chloroform.

For the self-assembly of the nanoparticle array, 350 μL of the nanoparticles dissolved in chloroform was casted on a water surface confined in a teflon ring. The array was transferred from the water surface to a Si chip with 150 nm thermally grown SiO_2 using a polydimethylsiloxane (PDMS) stamp. By this procedure, we produced two-dimensional, hexagonally ordered nanoparticle arrays with a lattice spacing of ~ 12 nm and an interparticle distance of ~ 2 nm, as shown in the scanning electron microscope (SEM) image and the sketch in Figure 1A,B.

Gold electrodes were patterned on the arrays using a shadow mask evaporation technique. The electrodes were evaporated at a distance of 8 μm on a 20 μm wide strip of nanoparticle array, leaving an $8 \times 20 \mu\text{m}^2$ sized electrically contacted nanoparticle array.⁹

Molecular Exchange. The incorporation of OPV into the nanoparticle array follows the method described in literature.¹⁵ The OPV-thiols with an acetylene protection group were dissolved in 2 mL of tetrahydrofuran (THF) to yield a 1 mM solution. The chip with the nanoparticle array was added to the vial and the vial was purged with Ar. Ten microliters of a 10% aqueous solution of ammonium hydroxide (NH_4OH) was added to remove the protection from the thiol groups of the OPV. The solution was kept under Ar atmosphere for 24 h. When the chip was removed, it was first washed in THF to remove nonbound OPV, then it was washed in ethanol, and after that it was blown dry with N_2 . This results in the interconnection of the Au nanoparticles by the OPV molecules as illustrated by the scheme in Figure 1B.⁷ The introduction of the OPV increased the conductance of the arrays by

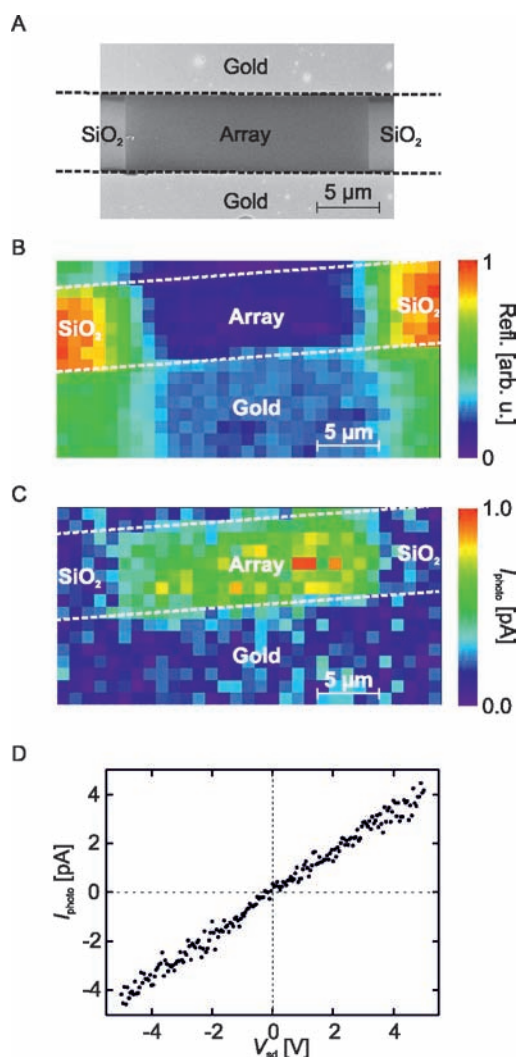


Figure 2. Two-dimensional photoconductance maps. (A) An SEM image of a nanoparticle array contacted by two gold electrodes; (B) the reflection signal of a laser beam when scanned over a nanoparticle array; white dashed lines indicate the border of the gold electrodes; (C) the simultaneously measured photocurrent I_{photo} . (B and C) $E_{\text{photon}} = 3.26$ eV, $I_{\text{opt}} = 1.6 \text{ kW cm}^{-2}$, $V_{\text{sd}} = 1$ V, and $f_{\text{chop}} = 1606$ Hz. (D) I_{photo} of a nanoparticle array as a function of V_{sd} measured with $E_{\text{photon}} = 3.35$ eV, $I_{\text{opt}} = 0.48 \text{ kW cm}^{-2}$, and $f_{\text{chop}} = 1533$ Hz.

approximately 1 order of magnitude as apparent from the conductance measurements before (circles) and after (open circles) the molecular exchange shown in Figure 1C. This and all of the following results were obtained on two sets of nanoparticle arrays, both of which were independently prepared. In total, our report relies on more than 20 contacted nanoparticle arrays. All results were highly reproducible between different arrays.

Photoconductance Measurements. Photoconductance measurements were performed under high vacuum conditions ($\sim 10^{-6}$ mbar) at room temperature. For optical excitation, we used a mode-locked titanium-sapphire laser with optical pulses of ~ 160 fs duration and a repetition rate of 76 MHz. To cover the UV spectral range, the frequency of the light was doubled using a BBO crystal. The visible spectrum was covered by supercontinuum generation in a nonlinear optical fiber and subsequent wavelength selection using diffraction filters. By means of a chopper wheel, the intensity of the optical excitation was modulated with a frequency f_{chop} . A DC bias V_{sd} was applied to the electrically

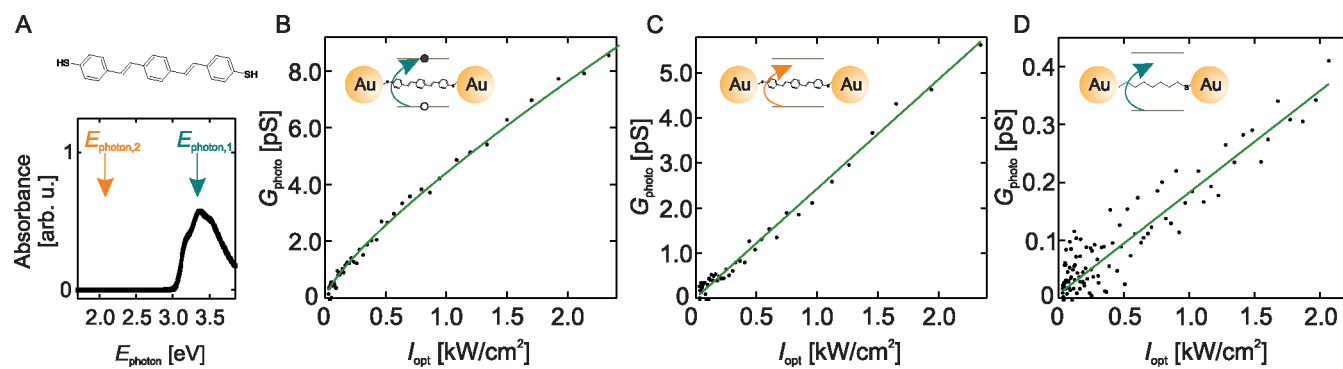


Figure 3. Photoconductance as a function of excitation intensity upon resonant and nonresonant irradiation. (A) The absorbance spectrum of the OPV molecule dissolved in THF. The two arrows indicate the photon energies used in presented experiments. (B) G_{photo} as a function of I_{opt} upon irradiation with light at $E_{\text{photon},1} = 3.35$ eV. The green line represents a fit to the data using eq 1. The inset schematically visualizes the resonant excitation of the OPV. (C) An identical measurement on the same sample using $E_{\text{photon},2} = 2.08$ eV. The green line represents a linear fit to the data. The inset visualizes the fact that the photon energy in this experiment is much smaller than the HOMO–LUMO gap of the OPV. In panel D, we show an identical measurement as in panel B performed on a sample only with octanethiols as linkers, but no OPV. A linear fit (green line) reproduces the data reasonably well. The inset represents the HOMO–LUMO gap of the octanethiol which is much larger than the energy of the photons used for excitation. (B–D) All are measured with $V_{\text{sd}} = 1$ V and $f_{\text{chop}} = 71$ Hz.

contacted nanoparticle array with a Yokogawa voltage source, and the resulting current was amplified in an Ithaco Model 1211 current–voltage converter. The optically induced current I_{photo} was determined as the current component at f_{chop} measured with an EG&G 7265 lock-in amplifier.

RESULTS

Spatially Resolved Photoconductance. To create a two-dimensional photoconductance map of our samples, we scan the laser beam with respect to the samples. We simultaneously measure the photocurrent and the intensity of the light reflected from the sample surface as a function of the current laser position. In Figure 2A, we show an SEM image of a nanoparticle array contacted by two gold electrodes. The structure can be easily recognized in the two-dimensional reflection map shown in Figure 2B. We ascribe the strong contrast in the reflection image to interference effects, since the relative reflectivities of the different sample parts (SiO_2 , gold, nanoparticle array, gold covered nanoparticle array) change strongly with irradiation wavelength. From the reflection image, we can accurately deduce the position of the nanoparticle array. We observe a pronounced photocurrent when irradiating the area covered with nanoparticle array, as shown by the two-dimensional map of the photocurrent I_{photo} in Figure 2C. We detect no I_{photo} when the SiO_2 next to the nanoparticle array or the gold electrodes themselves are irradiated. As shown in Figure 2D, we find that I_{photo} depends linearly on the bias voltage V_{sd} with no offset at zero bias. Therefore, the optoelectronic response can be described by an optically induced conductance G_{photo} , defined as

$$G_{\text{photo}} = I_{\text{photo}}/V_{\text{sd}}$$

In previous work,⁹ we have identified the photoconductance of arrays of octane coated nanoparticles to be caused by a bolometric conductance enhancement. Here, we will show that on resonant excitation of the OPV molecules we observe a photoconductance effect which appears in addition to the bolometric photoconductance.

Power Dependence of the Photoconductance. In Figure 3A, we plot the absorbance spectrum of OPV molecules dissolved in

THF. The molecules are transparent for photon energies E_{photon} below 3 eV. For a photon energy of 3.4 eV, the absorbance reaches a maximum due to a resonant excitation of an electron in the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).¹⁶ The blue arrow in Figure 3A indicates a photon energy of 3.35 eV used for the measurement shown in Figure 3B. Here, we plot the photoconductance as a function of light intensity measured on a nanoparticle array with OPV incorporated. The energy of the photons in this measurement is resonant with the HOMO–LUMO transition of OPV as it is schematically depicted in the inset. We observe a sublinear increase of the photoconductance for small light intensities and a linear increase at higher intensities. We interpret this behavior to be caused by the sum of two effects: A bolometrically induced conductance which increases linearly with the irradiation intensity and a sublinear contribution. The sublinear contribution to the photoconductance vanishes for all $E_{\text{photon}} < 3$ eV (only shown for $E_{\text{photon}} = 2.08$ eV). In Figure 3C, we show G_{photo} as a function of the irradiation intensity I_{opt} at $E_{\text{photon}} = 2.08$ eV (orange arrow in the absorption spectrum in Figure 3A). At this photon energy, the surface plasmon excitation of the nanoparticles in the array are excited. We find a strictly linear dependence of G_{photo} on I_{opt} consistent with a bolometrically induced conductance as previously described.⁹ The conductance behavior is the same for all $E_{\text{photon}} < 3$ eV. On the basis of these observations, we ascribe the sublinear increase of G_{photo} to the resonant excitation of the OPV molecular transition.

We note that, at 3.35 eV, we are not only resonant with the OPV molecular transition, but also with an interband transition of gold.¹⁷ However, we can rule out the excitation of gold as the cause for the nonlinear increase of the photoconductance. In Figure 3D, we present a measurement of G_{photo} as a function of I_{opt} on an identical array which was fabricated without the molecular exchange step. In such arrays, the nanoparticles are only interlinked by octanethiols. The interband transition in the gold upon irradiation with $E_{\text{photon}} = 3.35$ eV can also lead to a temperature increase in the nanoparticle array (see Supporting Information). Hereby, we interpret the linear dependence of the photoconductance on excitation intensity also at this photon energy to be caused by a purely bolometric effect.⁹

Frequency Domain Photoconductance Analysis. In our experiments, the intensity of the optical excitation is modulated using an optical chopper. By this, the irradiation of the sample is constantly switched on and off with the frequency f_{chop} . This provides access to another physical parameter of the observed effect, namely, the typical response time of the photoconductance. In Figure 4A,B, we show G_{photo} as a function of I_{opt} measured with a modulation frequency of $f_{\text{chop}} = 71$ and 721 Hz, respectively. Both measurements are performed on an array with OPV incorporated and at $E_{\text{photon}} = 3.35$ eV resonant with the molecular transition. Generally, the increase of G_{photo} with I_{opt} is nearly linear at large f_{chop} (Figure 4B), while it is sublinear for small f_{chop} (Figure 4A). In addition, we observe a distinctively smaller G_{photo} for increasing f_{chop} . Therefore, we conclude that the sublinear increase of G_{photo} is suppressed at high f_{chop} . From a series of measurements at different f_{chop} , we can deduce the response time of the resonant photoconductance to be on the order of milliseconds, as it will be discussed below in detail.

In summary, we observe a photoconductance mechanism which is only present upon resonant excitation of the OPV molecules incorporated in the nanoparticle arrays. The most prominent feature of this photoconductance mechanism is its sublinear dependence on the irradiation intensity I_{opt} . We determine the response time of the mechanism to be on the order of milliseconds. In the following, we discuss two models which can account for the observed behavior.

DISCUSSION

A lower limit of the response time of a photoconductor is set by the lifetime of the excited charge carriers. In organic molecules though, the excitation lifetime is much shorter than the observed millisecond response time.¹⁸ The optoelectronic response time, however, can be significantly increased by the presence of trap states.¹⁹ We propose two models based on trap state dynamics to describe our observations. Model A is based on a theory originally proposed by A. Rose to describe the behavior of semiconductor photodetectors.²⁰ Therein, the optically excited charge carriers directly increase the charge carrier density and thus lead to a photoconductance. Then, the filling of trap states leads to a decrease of the charge carrier density and the photoconductance. In contrast, in model B, the photoconductance is caused by the trapping of charge carriers in trap states. It follows the argumentation of Nakanishi et al., where the trapped carriers lead to an increase of the charge carrier density on the gold nanoparticles and thus to an increased conductance of the arrays.¹¹ The two models are compared below. We would like to note that our photocurrent spectroscopy does not allow to identify and further characterize the trap states, which are possibly located at the surface of the nanoparticles.¹¹ A further ingredient of the proposed models is a bolometrically induced photoconductance, as recently discussed in ref 9. Most importantly, this bolometric effect applies for an optical excitation of both the plasmons in the nanoparticle arrays and the interband excitations of the gold (see Supporting Information).

Model A. The model proposed by A. Rose is based on the filling of trap states to describe a sublinear increase of G_{photo} with I_{opt} in semiconductor photodetectors.²⁰ In this model, the photocurrent comprises charge carriers excited across an energy band. This process is linear with the irradiation intensity. However, the excited charge carriers can be trapped by localized states in the band gap. Filling of such trap states leads to a

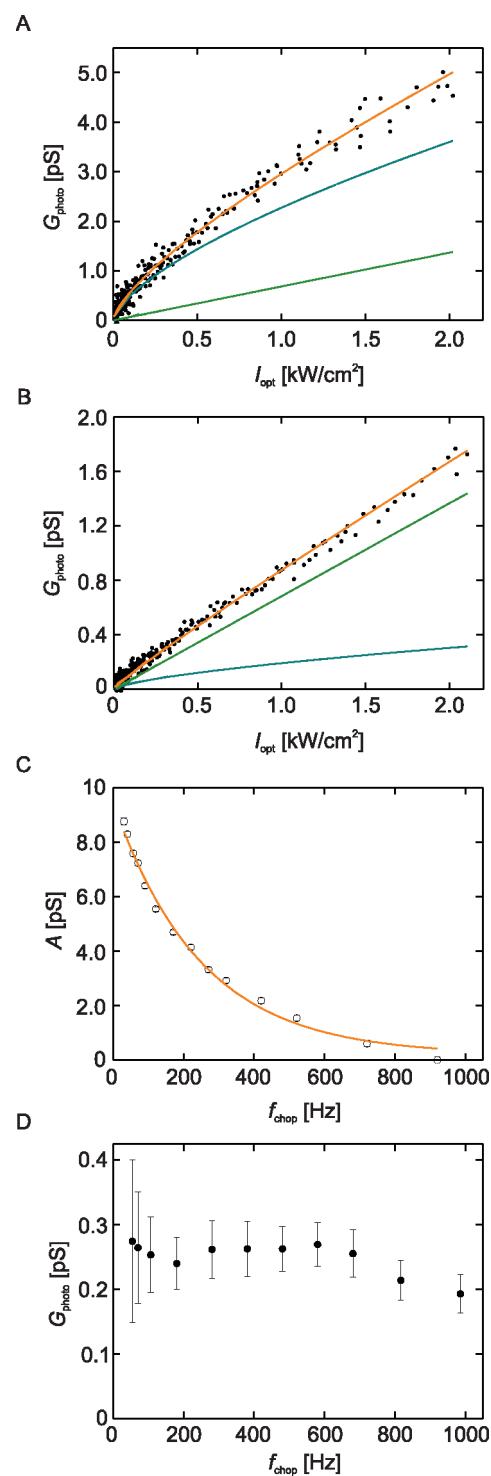


Figure 4. Frequency domain photoconductance analysis. (A and B) The photoconductance as a function of irradiation intensity with $E_{\text{photon}} = 3.35$ eV, $V_{\text{sd}} = 1$ V, and $f_{\text{chop}} = 71$ Hz and (B) $f_{\text{chop}} = 721$ Hz is shown. Orange lines represent fits to the data using eq 1, blue and green lines represent the first and the second term of eq 1, respectively. The linear contributions in panels A and B have the same slope. (C) The prefactor A of the sublinear contribution in 1 as a function of f_{chop} is shown. The orange line represents an exponential decay fitted to the data with a decay constant of 4.0 ms. (D) G_{photo} as a function of f_{chop} measured on an array with only octanethiols as linkers ($E_{\text{photon}} = 3.35$ eV, $I_{\text{opt}} = 1.6$ kW cm⁻²) is shown.

decrease of the lifetime of the additionally excited charge carriers. The combination of linear increase of the charge carrier generation and decrease of their lifetime leads to a power law dependence of G_{photo} on I_{opt}^{20} . This effect adds to a bolometrically induced conductance²⁰ and results in the following equation:

$$G_{\text{photo}} = A(I_{\text{opt}})^{\alpha} + BI_{\text{opt}} \quad (1)$$

where A is a constant describing the magnitude of the sublinear photoconductance. The exponent α is linked to the distribution of the trap states in the band gap. It lies between 0.5 and 1. The parameter B describes the magnitude of the bolometrically induced conductance.

Applying eq 1 to a set of 14 measurements at different modulation frequencies, we obtain a very good agreement between the data and the fitting functions, as is illustrated by the two fits (orange line) shown in Figure 4A,B. We find that at low f_{chop} , the photoconductance is dominated by the sublinear term in eq 1 (blue line in Figure 4A) which is associated with the resonant excitation of the OPV. The measurement with $f_{\text{chop}} = 721$ Hz shows a much weaker resonant photoconductance (blue line in Figure 4B). Here, G_{photo} is dominated by the bolometric effect (green line). In Figure 4C, we plot the magnitude of the resonant photoconductance A as a function of f_{chop} . We find a strong suppression of A for increasing f_{chop} . Fitting an exponential decay to the data, we determine the typical time constant of the resonant photoconductance to be 4.0 ms. Most importantly, all other fitting parameters are independent of f_{chop} . This means that there is no modulation frequency dependence of α with $\alpha = 0.664 \pm 0.006$ in all fits. This is consistent with the interpretation that α is determined by the trap state distribution and is therefore not influenced by f_{chop} . Also, we find no variation of the bolometric photoconductance for different f_{chop} with $B = 0.68 \pm 0.04$ pS cm² kW⁻¹. This is in agreement with measurements on samples without OPV inserted as shown in Figure 4D. There, we also find no dependence of G_{photo} on f_{chop} in the experimentally accessible frequency range.

Model B. In an experiment similar to the one described here, Nakanishi et al. observe an increase of the conductance of a nanoparticle array with noncharged ligands upon nonresonant irradiation.¹¹ They also find a response time of their sample on the order of 10–100 ms which they attribute to trap state dynamics of their system. They argue that the irradiation promotes electrons in the nanoparticles to higher energy which in turn fill up trap sites on the nanoparticle cores. The so-caused reduction of available trap sites leads to an increased electron density and thus to an increased conductance of the sample. The resulting photoconductance is roughly proportional to the number of trapped electrons.

We want to point out two major differences between our experiment and the one in ref 11. (i) We resonantly excite a molecular transition, therefore, promoting an electron on the molecule rather than on the nanoparticle core to an excited state. This leaves us with a limited number of possible excitations due to the small number of electrons per molecule. (ii) We use much higher irradiation intensities than those reported by Nakanishi et al. These two facts suggest that in our experiment we can reach the limit where a major part of the trapping sites is filled. In our model, the depletion of trapping sites leads to a saturation of the photoconductance and thus to the observed sublinear dependence of the photoconductance on irradiation intensity, as will be explained in the following.

We start with a rate equation relating the change in the trapped carrier population to the microscopic trapping and release rates:

$$\frac{dp}{dt} = k'_1(1-p) - k_2p \quad (2)$$

Here, $p(t) = n_t(t)/N_t$ is the time dependent portion of filled traps, with $n_t(t)$ the number of filled traps and N_t the total number of traps. The parameter k'_1 is the trapping rate of optically excited charge carriers. For simplicity, we assume a linear relation between excitation and trapping rate. Thus, we can write $k'_1 = I_{\text{opt}}k_1$. The release rate of the trapped carriers k_2 is independent of the irradiation intensity. The first term on the right-hand side of eq 2, which is proportional to the portion of free trapping sites $(1-p)$, describes the growth of the trapped carrier population due to irradiation. The second term describes the release of trapped carriers. The given rate equation integrates to

$$p(t) = \frac{I_{\text{opt}}k_1}{I_{\text{opt}}k_1 + k_2} (1 - e^{-(I_{\text{opt}}k_1 + k_2)t}) \quad (3)$$

Equation 3 consists of two parts. The first term describes the equilibrium between filled and empty traps which can be reached at a given irradiation intensity. It approaches unity for $I_{\text{opt}}k_1 \gg k_2$. The second term describes the time evolution of the trapped carrier population when the irradiation is switched on at $t = 0$. The filling of the traps has an intensity dependent time constant $\tau_0 = 1/(I_{\text{opt}}k_1 + k_2)$. In our experiment, the irradiation time t is given by the inverse chopper frequency. As a result, we can fit our data with the following function:

$$G_{\text{photo}} = A' \frac{I_{\text{opt}}k_1}{I_{\text{opt}}k_1 + k_2} (1 - e^{-(I_{\text{opt}}k_1 + k_2)/f_{\text{chop}}}) + B'I_{\text{opt}} \quad (4)$$

with A' a fitting constant relating the portion of trapped charge carriers to the induced change in conductance and B' the increase of the conductance due to the bolometric conductance enhancement.

Again, we obtain a good agreement between fit and measurement, as is illustrated by the two measurements shown in Figure 5A,B. Here, we plot the same data as in Figure 4A,B. Now, the orange line represents a fit to the data using eq 4, while the blue and green lines represent the first and second term in eq 4, respectively. Applying eq 4 to the before mentioned set of measurements with different modulation frequencies, we obtain a global set of parameters summarized in Table 1.

In this model, the amplitude of the resonant photoconductance A' is independent of f_{chop} . This is a consequence of the intensity dependent time constant $\tau_0 = 1/(I_{\text{opt}}k_1 + k_2)$. Because of this, at large f_{chop} , the resonant photoconductance is not suppressed, but it only reaches the saturation value at very high irradiation intensities. However, such high irradiation intensities cannot be applied to the sample due to irreversible changes in the nanoparticle arrays upon very high intensity irradiation. The resonant character of the photoconductance is expressed by the dependence of the fitting parameter k_1 on E_{photon} . In particular, k_1 decreases from 390 ± 44 cm² kJ⁻¹ at $E_{\text{photon}} = 3.35$ eV to 45 ± 4.5 cm² kJ⁻¹ at $E_{\text{photon}} = 3.22$ eV to zero at $E_{\text{photon}} = 2.82$ eV (data and fits not shown). In addition, we apply eq 3 to results obtained from samples having only octanethiols as linkers. There, we get as a result that k_1 is zero for all E_{photon} and all f_{chop} (e.g., linear fit in Figure 3D).

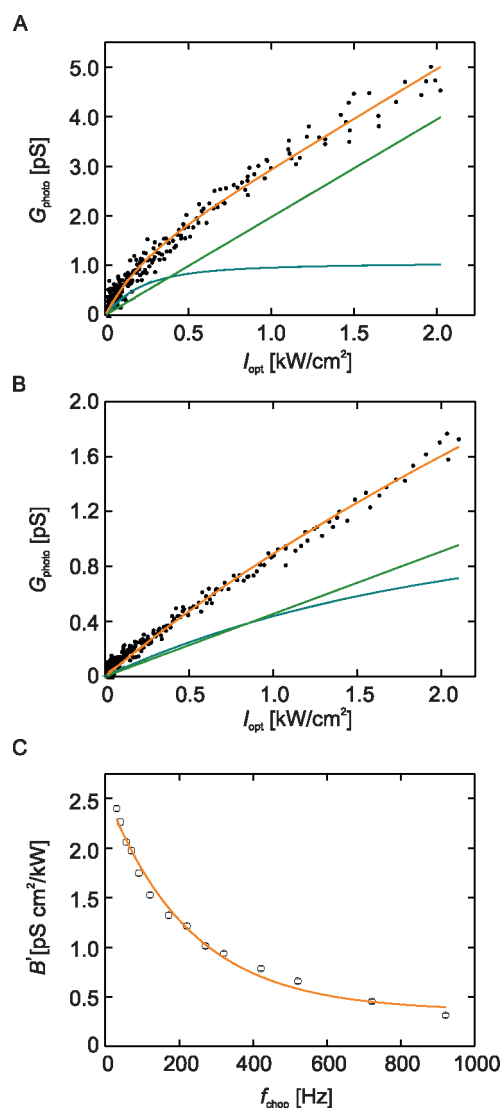


Figure 5. Depletion of trap states. (A and B) G_{photo} as a function of I_{opt} with (A) $E_{\text{photon}} = 3.35$ eV, $V_{\text{sd}} = 1$ V, and $f_{\text{chop}} = 71$ Hz and (B) $f_{\text{chop}} = 721$ Hz. Orange lines represent fits to the data using eq 4, blue and green lines represent the first and the second term of eq 4, respectively. (C) The prefactor B' of the linear contribution in eq 4 as a function of f_{chop} . The orange line represents an exponential decay fitted to the data with a decay constant of 4.4 ms.

Table 1. Fitting Parameters from Fitting eq 4 to a Set of 14 Measurements with Different f_{chop}

parameter	value
A'	1.08 ± 0.05 pS
k_1	390 ± 44 cm ² kJ ⁻¹
k_2	50 ± 5 s ⁻¹

In contrast to our findings with model A, in model B, satisfactory agreement between data and fit can only be achieved assuming a frequency dependence of the bolometric photoconductance. Figure 5C shows the fitting constant B' as a function of modulation frequency. We observe a suppression of the bolometric conductance enhancement at high f_{chop} . The orange line represents an exponential decay fitted to the data. It reveals a time constant of 4.4 ms. This is in

strong contradiction to measurements with arrays containing only octanethiols (Figure 4D), where G_{photo} is independent of f_{chop} . Furthermore, in ref 9 we estimated the bolometric response to be faster than 250 μ s. Hereby, our observations strongly indicate that only model A sufficiently describes the resonant photoconductance of the OPV molecules in the nanoparticle arrays.

CONCLUSION

We investigated the photoconductance of OPV molecules incorporated in gold nanoparticle arrays. We observe a photoconductance with a sublinear dependence on the laser intensity. We identify the photoconductance to be caused by the resonant excitation of the molecular transition. This resonant photoconductance exhibits an optoelectronic response time of several milliseconds. Trap states in the overall system are very likely to cause such a slow response. We formulate two models to describe our observations. In model B, the photoconductance is ascribed to the trapping of optically excited charge carriers in trap states. Generally, the depletion of such trap states upon high intensity irradiation can lead to the observed sublinear increase of G_{photo} with I_{opt} . Using this model to describe our data, however, we have to assume a suppression of the bolometric photoconductance on a time scale of 4.4 ms to obtain satisfactory agreement between data and fit. This is in contradiction to measurements of the bolometric photoconductance on samples without OPV molecules.

In model A, the charge carriers which are optically excited in the OPV molecules directly participate in the current through the nanoparticle arrays. Filling of the trap states in the array leads then to a decrease of the carrier lifetime and by this to the observed sublinear dependence of G_{photo} on I_{opt} . Model A describes the measured data very well. It also reproduces the independence of the bolometric photoconductance of the modulation frequency. Therefore, we conclude that we observed the conductance of OPV molecules in their electronically excited state. Our measurements demonstrate that organic molecules in molecular junctions can be used as modules in optoelectronic devices. However, careful examination of the origin of the trap states will be necessary in order to increase the overall optoelectronic signal and the response time of the devices.

ASSOCIATED CONTENT

S Supporting Information. Calculated absorption spectrum and a brief discussion of the origin of the bolometric photoconductance. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author
holleitner@wsi.tum.de

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