Direct observation of photo-switchable quasi-bound states in a Graphene-Azobenzene-Au multilayer

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The perfect transmission of charge carriers through potential barriers in graphene (Klein tunneling) is a direct consequence of the Dirac equation that governs the low-energy carrier dynamics1–6. As a result, localized states do not exist in unpatterned graphene but quasi-bound states can occur for potentials with closed integrable dynamics7,8. Here, we report the observation of optically switchable quasi-bound states in unpatterned graphene placed onto a mixed self-assembled monolayer (mSAM) of photo-switchable molecules. Conductive AFM measurements performed at room temperature reveal strong current resonances, the strength of which can be reversibly gated on- and off- by optically switching the molecular conformation of the mSAM. Comparisons of the voltage separation between current resonances (∼70–120 mV) with solutions of the Dirac equation indicate that the radius of the scattering potential is ∼7 ± 2 nm with a strength ≥ 0.5 eV. Our results and methods provide a route toward optically programmable carrier dynamics and transport in graphene nano-materials.

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Predictions of resonant states in quantum Dirac billiards have spurred intense experimental interest exploring, for example, the quasi-bound states in nano-ribbon and the relationship they have with the classical integrability of the dynamics, as dictated by the geometry. A variety of different approaches were explored to create bound or quasi-bound states in graphene, including the definition of n-p-n regions using local gates. Direct etching or oxidation of graphene was also used to produce nano-ribbon or quantum dot like structures known to have unique transport properties. Other approaches, including adatom deposition or ion bombardment through masks, also been used to produce well-defined regions where the carriers experience strong confinement. Whilst these diverse approaches to obtain carrier confinement are very successful they are all system specific and, moreover, are inflexible in the sense that they require changes in the fabrication processes in order to modify the confinement strength and geometry. In contrast, in the present manuscript we demonstrate the local potential to optically reconfigure the potential landscape in graphene using a switchable method.

The samples investigated were graphene/azobenzene/Au heterostructure multilayers fabricated as described in the supplementary information. On a Au-surface with a 1.5 nm root-mean-squared (RMS) roughness we deposited a mixed self-assembled monolayer (mSAM) consisting of an azobenzene derivative (4-(1-mercapto-6-hexyloxy)-azobenzene) and spacer-molecules (6-mercaptio-1-hexanol), such as to prevent steric hindrance of the photo-mediated molecular conformation switching. X-ray photoemission spectroscopy was performed in order to characterize the mSAM (see supplemantay information - Fig. S1a-b). Azobenzene molecules are known to be photochromic, being able to reversibly switch their conformation from the thermodynamically stable trans-configuration to the metastable cis-configuration upon illumination with UV light at 365 nm. This optically induced photo-isomerisation is depicted schematically in Fig. 1a and results in a reduction of the length of the molecule from 1.90 nm to 1.45 nm and a significant change of the dipole moment. We performed contact angle measurements to confirm that the mSAM molecular configuration is indeed fully switched by illumination at 365 nm with a power density of 850 µWcm⁻² for about 50 minutes (see Supplementary Information - Fig. S2b). Results obtained from two different classes of samples are presented here; a reference sample consisting of an mSAM on Au substrate without graphene and an active sample in which a monolayer of mechanically exfoliated graphene was positioned on top of the mSAM to form the graphene/mSAM/Au
hybrid. In the remainder of the paper we refer to these two types of samples as the reference and active samples, respectively. The transport properties of all samples and the topography of the local conductivity were characterized at room temperature using c-AFM in contact mode in three configurations; (i) before illumination in which the azobenzene layer is in the trans-configuration, (ii) after illumination with UV-light (365 nm with 850 µWcm$^{-2}$ for 30 mins) to induce a metastable switch of the molecular conformation to the cis-configuration, and (iii) after photo-switching the mSAM back to the trans-configuration using white light illumination. A metal coated Pt-Ir tip was used to perform the c-AFM measurement to study the transport properties of both the reference (Fig. 1a) and active samples (Fig. 1d) with the mSAM in either the cis- and trans- configurations, transport being measured between the Au-layer and the c-AFM tip. The measurements were performed at constant voltage over a 200 × 200 nm scan area, with current-voltage characteristics (I-V) at well-defined positions on the sample surface. Fig. 1b shows typical local I-V measurements recorded from the reference sample in either trans (blue curves) or cis configurations (red curves). A typical current map recorded at $V = +10$ mV is also presented in Fig. 1c to illustrate the homogeneity of the conductivity response. Here, the characteristic feature size in the topography of the current map reflects the underlying grain size of the Au-electrode. A dramatic change of the local conductivity is observed upon switching the molecular conformation, the current increasing by $\sim 10\times$ when the mSAM is switched into the cis configuration. This behavior is expected, arising from the reduction of the molecular length and the subsequent lowering of the tunneling barrier length, as reported by other groups$^{20,21}$. Control experiments were performed on samples with graphene on a Au substrate (without azobenzene molecules), and no photo-switching behavior was observed as expected (see Supplementary Information - Fig. S2a-b).

Similar measurements were performed on the active sample and typical results are presented in Fig. 1d-f. As for the reference, the active sample also reveals a dramatic and reversible change of the conductivity upon switching the mSAM from the trans- to the cis-configuration, as seen in the red and blue traces as shown in Fig. 1e. However, in strong contrast to the reference sample, in the cis-configuration pronounced peaks are observed in the I-V characteristics, with a typical voltage gap between the peaks of $\delta V_{gap} \sim 110 - 120$ meV. Such peaks in the local transport characteristics are only observed in the active sample, and only when the mSAM is switched into the cis-configuration, vanishing when the sample is
switched back to the *trans*-configuration (see green curve in Fig. 1e). Notably, the increase of current in the active sample from *trans-* to *cis*-configuration is now $\sim 100\times$ stronger. The current map of the active sample recorded at $+10$ mV (in the *trans*-configuration) reveals terraces with rings of high current, delineating the grains of the underlying Au-electrode, in strong contrast to our observations for the reference sample (Fig. 1f).

The peak to valley ratio of the current resonances observed in the *cis* I-V characteristics of the active sample was found to be dependent on the exact position of the c-AFM tip on the surface. This is shown in Fig. 2a that compares several different I-V traces, plotted on a linear scale and recorded at different locations on the sample surface, as indicated by the circles on the current map image (Fig. 2b), and recorded after UV exposure. Pronounced current resonances are observed in all the I-V characteristics in this *cis*-configuration with peak spacing ranging from 70 to 104 mV, superimposed on an approximately linear background, increasing with bias voltage. Measurements were performed on different locations on the grains in the graphene/mSAM/Au hybrid, universally showing the presence of pronounced current oscillations only when the mSAM is in the *cis*-configuration. Note that the amplitude of the current peaks in Figs. 1 and 2 is clipped to a maximum of 20 nA due to the current compliance of the amplifier used in the c-AFM. Upon executing consecutive up and down voltage sweeps we observed weak, but clear hysteretic effects as shown in Fig. 2c. Clear strong resonances are observed in the current, with peaks being rigidly shifted by $|\Delta V| \sim 3 - 12$ mV between successive sweeps, with respect to the previous trace. This observation is indicative of voltage induced fluctuations in the local potential in the graphene layer.

We identify the resonances in the I-V characteristics as arising from tunneling through quasi-bound states in graphene induced by the interaction with the mSAM via the disordered landscape provided by the $\sim 20 - 80$ nm sized grains in the Au electrode. To support this interpretation we performed simulations of the quasi-bound states in graphene based on the 2D Dirac equation with a circular gated region, within which a potential perturbation is applied (see supplementary material). The potential perturbation mediated by the mSAM most likely arises from the interaction of specific, particularly electronegative groups in the mSAM with the graphene, such as the $N=\equiv N$ bond linking the azobenzene derivative that interacts with the graphene much more strongly in the *cis*-configuration, as the dipole moment changes with conformation\textsuperscript{22}. This potential perturbation can be described over a
finite-sized circular region, \( H_V = V \vartheta (R - r) \), where \( V \) represents the potential strength of the gated region, and \( \vartheta \) is the Heaviside function determining the radius \( R \) of the region. Assuming the potential to be smooth such that it does not cause intervalley scattering, one can treat the problem at each Dirac point independently. The eigenvalue problem becomes \( \hbar v_F (\sigma_x p_x + \sigma_y p_y) \psi = (E - V \vartheta (R - r)) \psi \), where \( \psi \) is a spinor in the pseudospin basis, and \( \sigma \) are Pauli matrices. The cylindrical symmetry of the problem allows one to use a partial wave decomposition, so that the phase shifts gained by each angular momentum channel during the scattering process are obtained analytically. The phase shifts can be directly related to differential, total and transport cross sections, which reveal different aspects of the scattering processes, including the formation of quasi-bound states in the scattering region.

Figure 3 shows a characteristic \( V \) vs \( E \) map of the total cross section for this problem. High amplitude peaks signal the presence of resonances in the scattering, indicating the formation of quasi-bound states in the gated region with finite life time characterized by the width of the peak. The appearance of such ‘shape resonances’ is a direct consequence of interference effects of waves scattering on the potential profile. The quasi-bound states can be seen as circulating inside the gated region, avoiding Klein tunneling for a finite time, given their scattering from the potential boundary at non-normal angles of incidence. The simple circular symmetry of the model is naturally reflected on the spatial symmetry of such resonances, as shown in Fig. 3b. Notice that at high energy these shape resonances would mimic the classical whispering gallery modes inside the region defined by the potential. In that limit, one can understand the near-constant energy spacing between consecutive resonances, as the characteristic wavelength \( \lambda \simeq 2\pi R/n \), so that \( k_n = 2\pi/\lambda_n \), which would yield \( \Delta E = \hbar v_F (k_{n+1} - k_n) \simeq \hbar v_F/R \). For \( \Delta E \simeq 100 \text{ meV} \), corresponding to the value \( e\delta V_{gap} \) observed in the experiments (Fig. 1), we estimate \( R \simeq 7 \text{ nm} \). Notice also that the resonances appear nearly symmetrically around zero energy in Fig. 3b, although they disappear for \( E \geq V \). Comparing this expectation with our experiments suggests that, when switched into the \textit{cis}-configuration, the mSAM provides a potential perturbation strength, which in this case is at least \( \sim 0.5 \text{ eV} \), and probably closer to 1 eV in most cases. As will be shown below, such large local shift of the neutrality point is consistent with micro Raman data recorded from our sample. It is important to notice that an irregular geometry would result in shorter lifetimes for the shape resonances, becoming increasingly short-lived at higher energies (bias),
FIG. 1. Samples and measurement configurations. a, Azobenzene molecule in trans (elongated form) and cis (bent) configurations. The arrow illustrates the switching and resultant shortening of the effective molecular length. b, I-V transport characteristics at a fixed position on the reference sample before and after switching from trans (blue curve) to cis (red). c, Typical current map of 200 × 200 nm region in the trans-configuration with a fixed bias voltage of 10 mV. d, Schematic representation of c-AFM measurement on the graphene/mSAM/Au hybrid. e, Typical I-V characteristics in trans-configuration before illumination (blue trace), in cis-configurations after switching with UV-light (red trace) and after switching back to the trans-configuration (green trace) following white light illumination. f, Typical current topography over a 200 × 200 nm area at a fixed bias voltage of 10 mV with the mSAM in the trans-configuration. The current compliance used for all measurements was set to 20 nA.
FIG. 2. **Current resonances.** a, I-V characteristics measured on several positions of the sample. Colour of the I-V traces corresponds to the position on the current map recorded at fixed bias of 10 mV when the molecules are in cis-configuration. b, The switching of the molecules has been carried out by illuminating the sample with 360 nm lamp over a 30 min time span. c, Typical I-V traces recorded consecutively in up-down sweeps over an entire 2 sec time. Each trace is vertically shifted for clarity; the arrow indicates bias sweep direction. The resonance peaks are slightly shifted by few millivolts with respect to the previous cycle.

resonant state, extending over the region of the Au-azobenzene grains. Such experiments require high control of the tip drift and were not possible with the current setup; an improved experimental design would allow such images and will be reported elsewhere.

To gain more insight into the interaction of the mSAM with the proximal graphene overlayer, we performed Raman spectroscopy (Fig. 4a-b). This measurements provide information on the structural and electronic characteristics of graphene. In particular, one can use the Raman data as a signature of the defect density (D-band), the in-plane carbon \( sp^2 \) vibrational mode (G-band) and stacking orders (2D-bands). It has also been demonstrated by several groups\(^{25,27} \) that the frequency of the G and 2D Raman peaks, as well as their linewidth and the ratio of their intensity (\( I_{2D}/I_G \)), are dependent on the position of the Fermi level relative to the Dirac point. In the context of our experiments, such changes would reflect an effective doping of the graphene film induced by the interaction between the mSAM and graphene layer\(^{28} \).

Figure 4a compares typical Raman data recorded from pristine graphene and from the graphene/ mSAM/Au hybrid with the mSAM switched into cis- and trans- configurations.
FIG. 3. **Shape resonances in a circular region.** a, Map of total cross section, $\sigma_{total}$, for circular gated region of radius $R$, as function of gate potential $V$ and electron energy $E$ in units of $h\nu_F/R$ ($\sigma_{Total}$ scaled by $k = E R / h\nu_F$). Nearly periodic peaks in $E$ at constant $V$ are shape resonances with consecutive peaks characterized by $\Delta E \simeq h\nu_F/R$. b, Spatial amplitude map of a typical resonance at $E R / h\nu_F = -10.2$ for $V R / h\nu_F = 22.1$, resonant peaks in the cross section result in spatial amplitudes increasingly bounded to the perimeter of the circular gate region as $|E|$ increases, similarly to well-known whispering gallery modes.

Starting from pristine graphene (black spectrum) the ratio $I_{2D}/I_G$ is lowered to a value $1 < I_{2D}/I_G < 2$ for the graphene/mSAM/Au hybrid when the molecules are in trans (blue spectrum). Upon switching the mSAM to the cis-configuration (red spectrum), the intensity ratio $I_{2D}/I_G$ is even below one, indicative of a strong shift of the Fermi level from the Dirac point and significant interaction between the mSAM and the proximal graphene layer. Finally, upon switching the mSAM back from cis-configuration to trans-configuration, after illumination with white light for 40 min, we observe a near full recovery of the observed Raman signal (green spectrum). The drop in $I_{2D}/I_G$ suggests that the proximal mSAM results in a shift of the Fermi level induced by the azobenzene molecules already in trans and an even stronger perturbation in cis-configuration. We tentatively attribute the stronger interaction of the cis-mSAM with the graphene to the closer proximity of the nitrogen atoms when the azobenzene is in the compact cis form. Such analyses were performed on several positions on the sample. The shift of the Raman peaks provides further evidence
FIG. 4. Raman spectroscopy on graphene/$SiO_2$ and Graphene/Azobenzene/Au hybrid system. a, Raman spectrum recorded from a pristine graphene on $SiO_2$ (dark curve) when excited with 514.5 nm cw laser. The top spectra refers to the graphene when transferred on mSAM on Au substrate. The blue and green spectra refer to the case when the azobenzene molecules are in trans, while the red spectrum was recorded just after 30 min of UV exposure, when the azobenzene molecules are in cis. The switching back of the molecules was obtained by irradiating the sample with white light for 40 min. b, A zoom of the D-band highlights the change of the linewidth when the molecules switch from trans- to cis-configuration and back again to trans-configuration.

of doping from azobenzene in trans-configuration, since both the G and 2D bands are blue-shifted with respect to the reference sample by about 4–8 cm$^{-1}$. Although it is difficult to have information about the type of doping, because both p- or n-doping would lead to a stiffening of vibrational modes, the Raman shift suggests an effective local charging of graphene of approximately 1.2–2×10$^{13}$ cm$^{-2}$ and a corresponding shift of the Fermi level of $\approx$ 0.4–0.5 eV. In Fig. 4b a zoom of the D-band highlights the change of the linewidth when the molecules switch from trans- to cis-configuration and back again to trans-configuration.

In summary, we have presented experimental evidence for the direct observation of quasi-bound states in a graphene single layer system, formed by reversible switching of the interaction with a functional substrate, in this case an optically switchable mSAM-Au-electrode. The functionalization of the substrate underneath graphene enables the reversible modification of the electrical and quantum properties of the Dirac fermions. Such variation is obtained by using aromatic photochromic molecules that change their configuration upon
illumination with UV light. We demonstrate that when the molecules are in the compact cis form, the stacking and molecular dipole effectively gate a region in the nearby graphene layer. This hybrid assembly allows for possible in situ modification of scattering potentials on graphene using a convenient method - simply illuminating to change the conformation of the proximal mSAM in a controllable fashion.

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