### Supporting Information

# Ultrafast Bidirectional Charge Transport and Electron Decoherence At Molecule/Surfaces Interfaces: A Comparison of Gold, Graphene and Graphene Nanoribbon Surfaces

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Contents:

- 1. Measurement Details and Sample Preparation
- 2. XPS and NEXAFS Measurements
- 3. DFT Calculations for NEXAFS spectra
- 4. The RPES Measurements
- 5. The RPES Core-Hole-Clock Method with Charge Transfer from the Substrate
- 6. References

#### 1. Measurement Details and Sample Preparation

The experiments were conducted at the ALOISA beamline of the Elettra Synchrotron in Trieste. The measurement chamber was maintained at an ultrahigh-vacuum at pressures of  $10^{-10}-10^{-11}$  mbar.<sup>1-3</sup> The 4,4'-bipyridine (BP) molecules were purchased from Sigma-Aldrich (purity >99%) and used without further purification. The molecules were placed in a Pyrex cell and connected to the pre-chamber through a leak valve.

The Au(111) surface was prepared by cycles of Ar+ sputtering and annealing at 400 K. Xray photoemission spectroscopy (XPS) was used to check for any chemical impurities (O, N, and C). The BP cell was heated to several tens of degrees above room temperature and BP was leaked into a pre-chamber to maintain a partial BP pressure of 10<sup>-7</sup> mbar for 4 - 5 minutes. The sample was cooled to -65° C for the multilayer phase, and it was kept at room temperature for the monolayer phase.

The epitaxial graphene on Ni(111) surface was prepared by repeatedly sputtering (Ar+, 2keV) and annealing (900K) the Ni(111) surface. XPS and Helium atom scattering were used to check for the presence of any chemical impurities and to probe the surface order. Epitaxial graphene was prepared via catalytic dissociation of ethylene on Ni(111) surface. An ethylene partial pressure of  $10^{-6}$  mbar was maintained for 60 minutes while keeping the surface at 850K.<sup>4</sup> The graphene film was probed using XPS and ultraviolet photoemission spectroscopy with He II line at 40.8 eV. Examination of the graphene  $\pi$ -band bottom, close to  $\Gamma$ , was used to identify the graphene layer as epitaxial graphene.<sup>4</sup> The epitaxial graphene/Ni(111) sample was exposed to ambient conditions before being transferred to the ALOISA chamber. The sample was annealed

in the ALOISA chamber at 500 K to recover the pristine graphene. XPS, valance band photoemission spectroscopy and near edge X-ray absorption fine structure (NEXAFS) spectroscopy measurements were further performed to characterize the epitaxial graphene/Ni(111) sample. To create the BP self-limiting monolayer film, a partial BP pressure of  $10^{-7}$  mbar was maintained in the pre-chamber for 3 minutes, while the sample was cooled to - 50° C.

Graphene nanoribbons (GNR) were formed depositing 10,10'-dibromo-9,9'-biantryl (AOKBIO, 98+% purity) on the cleaned Au(111) sample maintained at 200C to ensure saturating the Au(111) surface with the GNR precursor. This surface was then annealed to 400C to create GNRs as described previously.<sup>5</sup> XPS and NEXAFS measurements were performed to characterize the GNR film on the Au(111) surface. To create the BP monolayer film, a partial BP pressure of  $10^{-7}$  mbar was maintained in the chamber for 5 minutes while the sample was cooled to -45° C.

## 2. X-ray Photoemission Spectroscopy and Near Edge X-ray Absorption Fine Structure Spectroscopy Measurements

X-ray photoemission spectroscopy (XPS) measurements were performed at the ALOISA beamline with the X-ray beam at grazing-incidence (4°) to the sample. Photoelectrons from the sample were collected at the normal to the surface using a hemispherical electron analyzer with an acceptance angle of 2°, and an overall energy resolution of ~ 0.2 eV. The energy scale for XPS spectra was calibrated by aligning the Au  $4f_{7/2}$  peak to a binding energy of 84.0 eV for the Au(111) and GNR on Au(111) measurements. For the epitaxial graphene on Ni(111), XPS spectra were aligned to the Fermi level.

Near edge X-ray absorption fine structure (NEXAFS) measurements were performed on the nitrogen K-edge by sweeping the incident photon energy from 396 eV to 420 eV in steps of 0.1 eV. The photon incidence angle was set to 6°. Spectra were acquired using a channeltron detector with a wide acceptance angle in the partial electron yield mode and a high pass filter with cutoff energy set to 370 eV. The photon flux was monitored on the last optical element along the beam path. The sample normal was oriented either parallel (p-pol) or perpendicular (s-pol) to the light polarization (s-pol).

The relative intensity of the NEXAFS signal in s-pol and p-pol for the N1s to LUMO transition was used to obtain the orientation of the aromatic ring relative to the surface. The angle  $\theta$  of the ring to the surface is determined as  $\tan(\theta) = \sqrt{2I_s/I_p}$  where  $I_s$  and  $I_p$  are the intensities of the LUMO NEXAFS peak from the *s-pol* and *p-pol* spectra respectively.

#### 3. DFT Calculations for NEXAFS Spectra

We calculate the nitrogen K-edge spectra using GPAW, a grid-based real-space projectoraugmented-wave (PAW) code, with the BLYP exchange-correlation functional<sup>6, 7</sup>. For these simulations, isolated molecules were first relaxed to their optimized geometries. Default grid spacings and convergence thresholds were employed. All NEXAFS calculations were performed using the half-core-hole approximation<sup>8</sup>. The absolute energy scale was determined by performing a delta Kohn-Sham calculation and shifting the calculated spectrum using the calculated total energy difference between the ground state and the first core excited state.



SI Figure 1. The measured magic-angle N K-edge NEXAFS spectrum (blue) for bipyridine on Au(111) compared with the calculated absorption spectra (dashed red) in the transition potential approximation. The calculated peaks with the highest transition probabilities are indicated and assigned accordingly.

#### 4. The RPES Measurements

The RPES spectra at the nitrogen K-edge were obtained by taking XPS scans spanning 0-60 eV binding energy range with the photon energy tuned between 394 eV and 423 eV in steps of 0.2 eV and 0.5 eV for all surfaces studied. RPES measurements for charge transfer time calculations were performed in magic angle conditions, with the light polarization and the electron analyzer at 54.7° with respect to the surface normal. This yielded a RPES signal that was independent of the molecular orientation on the sample. For the angle-dependent RPES measurements, the angle between the photon polarization and surface normal set to the values stated in the main text while the electron analyzer was always collinear with the photon polarization. These RPES data were then normalized and analyzed following previously published procedures.<sup>9, 10</sup> Briefly,

the photon flux on the last optical element along the beam path was measured and used to normalize and calibrate the RPES scans for any fluctuations in photon intensity and energy. The energy scale for XPS spectrum was calibrated as detailed above. The non-resonant photoemission spectrum was obtained from the XPS scan at 395 eV and subtracted from the entire RPES spectra. The RPES line scans were then further normalized by the overall Auger intensity which scales with the absorption cross-section at a given photon energy.



Electron Kinetic Energy (eV)

SI Figure 2. Nitrogen K-edge RPES maps of (A) BP multilayer on Au(111) (B) BP monolayer on Au(111), (C) BP monolayer on epitaxial graphene and (D) BP monolayer on GNR. The LUMO\* resonance scans are taken along the dashed black lines. The dashed orange lines indicate the energy used for the scans above the ionization edge.

In SI Figure 2, we show nitrogen K-edge RPES maps of a BP multilayer on Au(111) and a BP monolayer on Au(111), epitaxial graphene and GNR. We see the N1s to LUMO transition signature around photon energy of 399 eV. From these maps, we obtain the line scans that are shown in Figure 3 of the main text. The core-hole clock method described below is then used to determine the charge transfer time and the fraction of the LUMO<sup>\*</sup> that drops below the Fermi level in the monolayer systems.

#### 5. The RPES Core-Hole-Clock Method with Charge Transfer from the Substrate

In this section, we present the extension of the standard core-hole clock method<sup>11</sup> to obtain the bidirectional charge transfer time and the fraction of the LUMO\* that drops below the Fermi level from the RPES measurements.

In the core-hole clock method, a core electron is photoexcited to the LUMO, leaving a core-hole on the molecule; and the energy distribution of the subsequent electron emission is measured. The process relevant to the core-hole clock method is the filling of the core-hole and the subsequent emission of an electron, leaving the LUMO empty; this is denoted as the participator decay. In a coupled system, the participator decay gets quenched if the charge transfer to the substrate occurs within the core-hole life-time. Therefore, by comparing the participator decay intensity in the isolated and the coupled system, the charge transfer time in the coupled system can be determined as has been done before.<sup>11</sup> In the measurements presented here, when a core-hole is present, the LUMO\* is partially below the Fermi level and can thus get occupied due to a charge transfer from the substrate.

7

To determine the bi-directional charge transfer time, one needs to consider two types of decay process that will contribute to the participator decay intensity. First, there is a participator decay that occurs from the LUMO\* electron. Additionally, there is an Auger type participator decay (from the fraction of the LUMO\* that is below Fermi) that can occur after charge transfer from the LUMO\* to the substrate. Denoting the participator decay intensity as  $I_o$  in the isolated system and as  $I_c$  in the coupled system, we can get a relation between  $I_o$  and  $I_c$  as:

$$I_c = I_o \frac{\tau_{CT}}{\tau_{CH} + \tau_{CT}} + I_o x \frac{\tau_{CH}}{\tau_{CH} + \tau_{CT}}$$
(1)

where  $\tau_{CH}$  is the core-hole lifetime,  $\tau_{CT}$  is the charge transfer time, *x* is the fraction of the LUMO\* below the Fermi level. The first term in Eq. 1 is the standard expression that has been used before and is attributed to the photoemission type participator decay.<sup>11</sup> The second term is due to the Auger type participator decay that can occur only if the LUMO\* is partly below Fermi and charge transfer from the LUMO\* to the substrate has occurred. The process giving rise to the second term in Eq. 1 is identical to the Auger type participator decay occurring after the charge transfer from the substrate to LUMO\* following an excitation of a core electron above the ionization edge. We denote this process as the super-participator decay and its intensity (*l*<sub>s</sub>) is given by

$$I_s = I_o x \frac{\tau_{CH}}{\tau_{CH} + \tau_{BT}} .$$
<sup>(2)</sup>

Here,  $\tau_{BT}$  is the bi-directional charge transfer time.

Since the charge transfer time in both directions is equal, Eq. 1 and 2 can be solved to find x and  $\tau_{c\tau}$  which yields

$$\tau_{CT} = \tau_{CH} \frac{f(1-\beta)}{1 - f(1-\beta)} .$$
(3)

$$x = \frac{f\beta}{1 - f(1 - \beta)} \tag{4}$$

where f is  $I_c/I_o$  and  $\beta$  is  $I_s/I_c$ .

The equations above are valid when the light polarization is perpendicular to the nodal plane of the nodal plane of the molecular  $\pi$ -system. Therefore, we need to account for the fact that the molecular  $\pi$ -system makes a small angle with the substrate, as determined from NEXAFS measurements presented in the main text. We also need to consider the light polarization when comparing the Auger type super-participator intensities with photoemission type participator intensity since there is a clear angular dependence in the latter.

The photoemission type participator decay intensity is proportional to  $(\boldsymbol{\epsilon} \cdot \boldsymbol{n})^2$  where  $\boldsymbol{\epsilon}$  is the polarization unit vector and  $\boldsymbol{n}$  is the vector normal to the nodal plane of the molecular  $\pi$ system. We calculate the  $(\boldsymbol{\epsilon} \cdot \boldsymbol{n})^2$  as a function of  $\boldsymbol{\epsilon}$  and  $\boldsymbol{n}$  assuming that there is no azimuthal dependence on the molecular orientation on the surface. We use

$$\varepsilon = \sin(\theta) \hat{x} + \cos(\theta) \hat{z}$$
(5)

$$n = \sin\alpha\cos(\phi - \pi/2)\hat{x} + \sin\alpha\sin(\phi - \pi/2)\hat{y} + \cos\alpha\hat{z}$$
(6)

where  $\theta$  is the polar angle between the surface normal and the polarization unit vector,  $\alpha$  is the polar angle between the surface normal and the normal to the molecular  $\pi$ -system, and  $\phi$  is the azimuthal angle of the molecular  $\pi$ -system.

Averaging  $(\boldsymbol{\epsilon} \cdot \boldsymbol{n})^2$  over  $\phi$ , and using Eq. 5 and Eq. 6 we get:

$$\overline{(\varepsilon \cdot n)^2} = \frac{\sin^2 \theta \sin^2 \alpha}{2} + \cos^2 \theta \cos^2 \alpha \tag{7}$$

Since measurements are made at the magic angle ( $\theta = 54.7^{\circ}$ ),  $\cos^2\theta = \sin^2\theta/2$ , and thus the average ( $\boldsymbol{\epsilon} \cdot \boldsymbol{n}$ )<sup>2</sup> is independent of  $\alpha$ . We obtain:

$$I_{c}^{m} = I_{o}^{m} \frac{\tau_{CT}}{\tau_{CH} + \tau_{CT}} + \frac{I_{o}^{m}}{\cos^{2} \theta} x \frac{\tau_{CH}}{\tau_{CH} + \tau_{CT}}$$
(8)

$$I_s^m = \frac{I_o^m}{\cos^2 \theta} x \frac{\tau_{CH}}{\tau_{CH} + \tau_{BT}}$$
(9)

where  $I_c^m$ ,  $I_s^m$  and  $I_o^m$  are the measured intensities at the magic angle. Solving Eq. 8 and Eq. 9 yields,

$$\tau_{CT} = \tau_{CH} \frac{f(1-\beta)}{1-f(1-\beta)}$$
(10)

$$x = \frac{\cos^2 \theta f \beta}{1 - f(1 - \beta)} . \tag{11}$$

where f is  $I_c^m / I_o^m$  and  $\beta$  is  $I_s^m / I_c^m$ .

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