

## SUPPORTING INFORMATION

### Structural, Electronic, and Vibrational Properties of a Two-Dimensional Graphdiyne-like Carbon Nanonetwork Synthesized on Au(111): Implications for the Engineering of $sp$ - $sp^2$ Carbon Nanostructures

Andi Rabia<sup>a</sup>, Francesco Tumino<sup>a</sup>, Alberto Milani<sup>a</sup>, Valeria Russo<sup>a</sup>, Andrea Li Bassi<sup>a</sup>, Nicolò Bassi<sup>a</sup>;¶ Andrea Lucotti<sup>b</sup>, Simona Achilli<sup>c</sup>; Guido Fratesi<sup>c</sup>, Nicola Manini<sup>c</sup>, Giovanni Onida<sup>c</sup>, Qiang Sun<sup>d</sup>;⊥ Wei Xu<sup>d</sup>, Carlo S. Casari<sup>a\*</sup>

<sup>a</sup>Department of Energy, Politecnico di Milano via Ponzio 34/3, I-20133 Milano, Italy.

\* Tel: +39 0223996331; E-mail: [carlo.casari@polimi.it](mailto:carlo.casari@polimi.it)

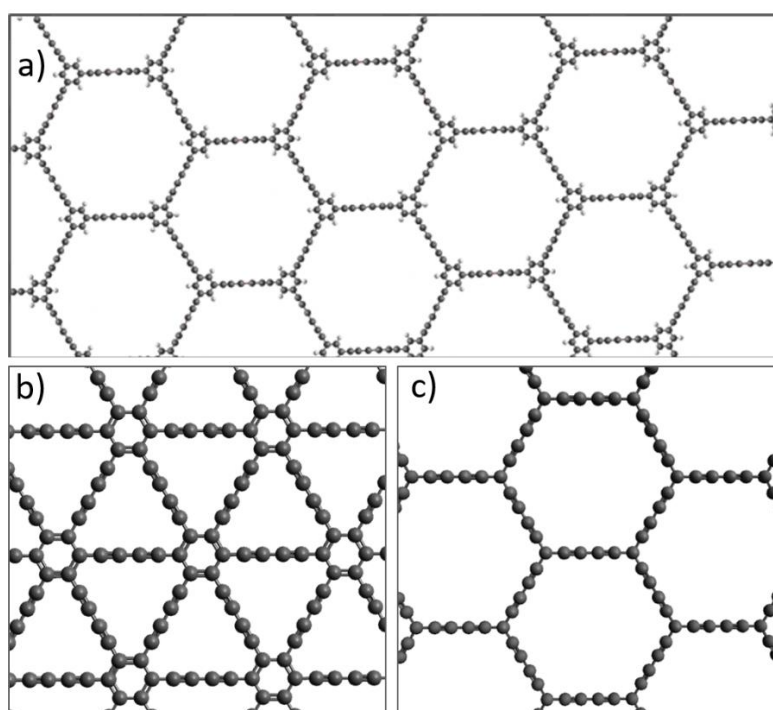
<sup>b</sup>Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy.

<sup>c</sup>ETSF and Dipartimento di Fisica "Aldo Pontremoli", Università degli Studi di Milano, Via Celoria, 16, I-20133 Milano, Italy.

<sup>d</sup>Interdisciplinary Materials Research Center, College of Materials Science and Engineering, Tongji University, Shanghai 201804, P. R. China.

¶ Present address: Empa, Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland.

⊥ Current address: Materials Genome Institute, Shanghai University, 200444 Shanghai, China.

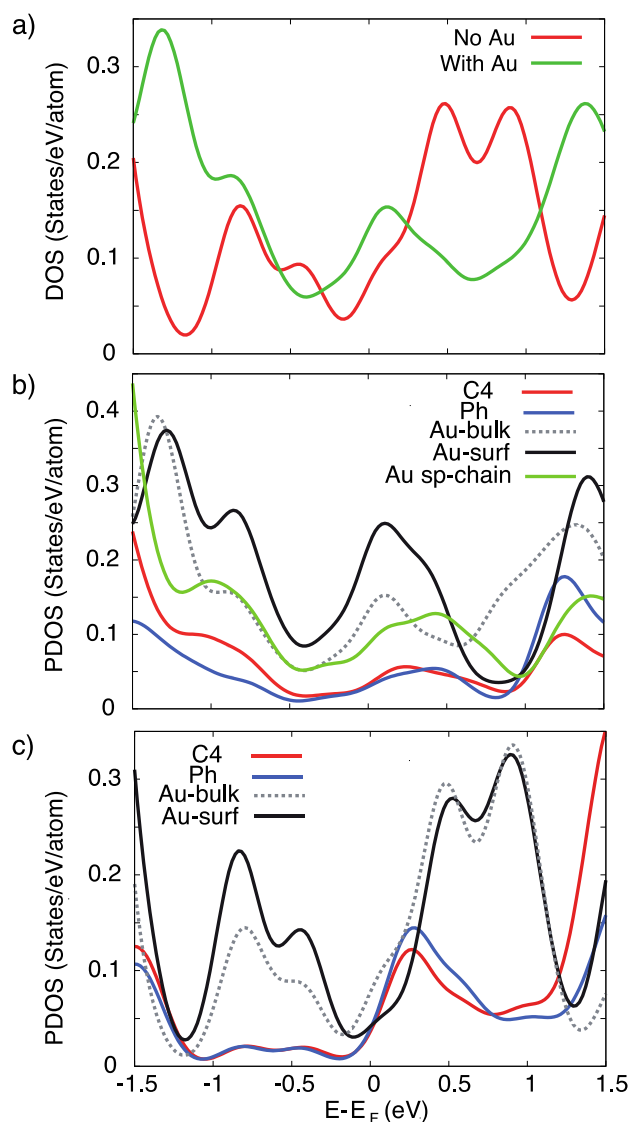


**Figure S1.** Structure of a) the graphdiyne-like system investigated in this work; b)  $\gamma$ - graphdiyne and c)  $\alpha$ - graphdiyne.

### Theoretical simulation of STS spectra

We simulated also the STS of the two 2D networks as the DOS at the  $\Gamma$  point, which is representative of the states with the maximum interaction with the tip due to their slow decay in vacuum.

The STS simulations of the metalated and C-C coupled systems, reported in Fig. S2 display relevant differences in the energy range around the Fermi level. In particular, the C-C coupled system is characterized by a feature between 0.5 eV and 1.0 eV which is absent in the metalated system. Differently, the overall contribution of the states below the Fermi level is larger for the metalated system due to the large feature between -1 eV and -1.5 eV. Moreover, the metalated system is characterized by a broad peak at the Fermi level.



**Figure S2:** a) Density of States at the  $\Gamma$  point for the metalated and C-C coupled nanonetwork. (b) and (c) Density of States at  $\Gamma$  projected on selected atoms and groups of the metalated and C-C coupled nanonetwork, respectively.

By considering the projection of the Density of States (PDOS) at the  $\Gamma$  point on different groups and atoms of the two systems (Fig. S2b and S2c), we are able to assign the most intense features in the STS simulation to states of the Au(111) substrate, while the molecular states contribute poorly to the total DOS at  $\Gamma$ . In particular, the feature at the Fermi level in Fig. S2b corresponds to

the Shockley state of Au(111), as confirmed by the different weight of this state on the surface (black line) with respect to atoms in the bulk (black dotted line). The upward energy shift of the Shockley state compared to the clean surface ( $E_B = -0.5$  eV) is due to the charge transfer from the substrate to the molecule. Indeed, the supported sp-sp<sup>2</sup> carbon nanonetwork displays a net increase of the valence charge that amounts to +0.68 electrons compared to the freestanding molecular overlayer. The charge transfer to the molecule is mainly directed to the carbon atoms while gold atoms in the chain are partially depleted of charge, donating 0.2 electrons.

In the C-C coupled system the interaction between the molecule and the substrate is small, leading to a negligible variation of the valence charge of the molecule (-0.012 e) compared to the freestanding overlayer. For the same reason, the electronic properties of the substrate are mildly modified upon adsorption and the binding energy of the Shockley state does not change.

### **Computational investigation of Raman Spectra: Methods and Models**

As reported in the main text, the experimental characterization of 2D sp-sp<sup>2</sup> carbon nanonetwork by means of Raman spectroscopy have been supported by Density Functional Theory calculations, carried out on different molecular models.

This approach has been successfully adopted also in a previous paper [1] on a similar system, offering a reliable interpretation of the experimental trends on the basis of peculiar molecular interactions. In the present case the computational investigation has been further extended, to test molecular models which could better approach the real system.

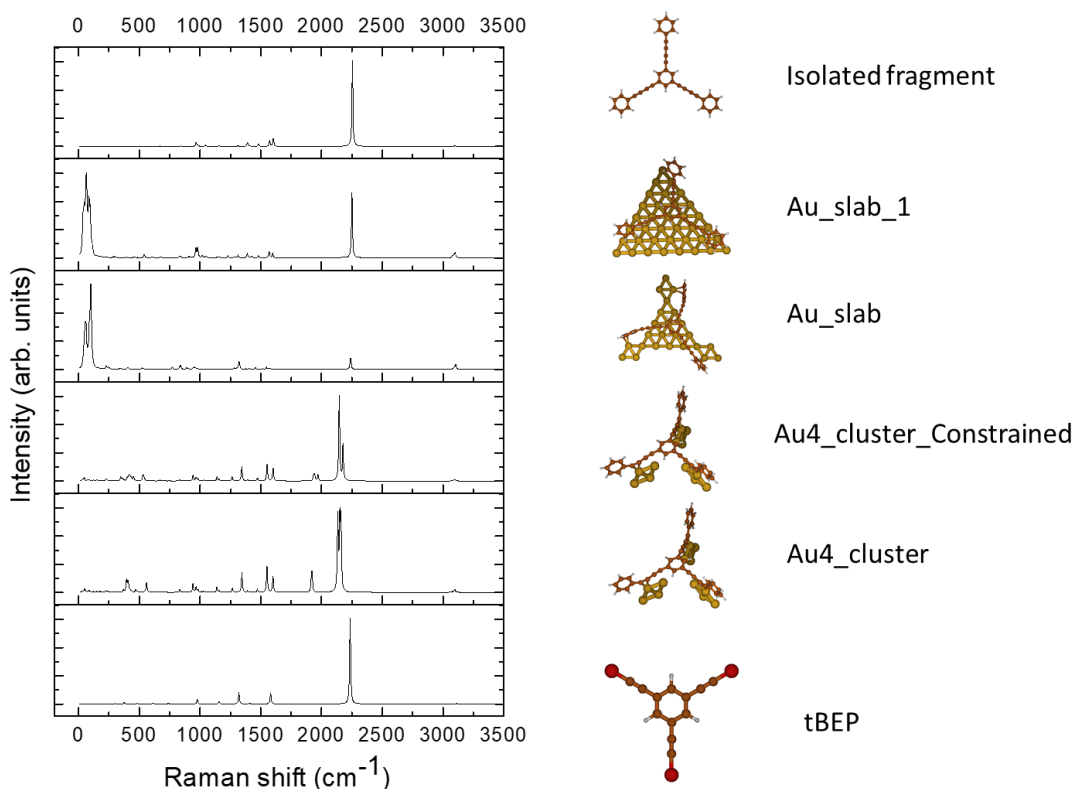
Modeling the present system is indeed far from being trivial: the extended 2D sp-sp<sup>2</sup> carbon sheet is interacting with Au surface and the closest model would require a calculation where periodic boundary conditions are introduced to describe an infinite, periodic 2D crystal. However, the simulation of both vibrational wavenumbers and Raman intensity is not so easily affordable by using common plane-wave pseudopotentials DFT methods, since hybrid exchange-correlation functionals would be also needed for an accurate prediction of the spectral pattern. On the other hand, adopting hybrid functionals together with a Gaussian function basis set does not allow to deal with the infinite Au slab, due to the occurrence of many convergence problems and linear dependencies in the solution of the electronic problem. Moreover, the weak interaction with the Au surface cannot be described accurately by DFT methods.

In order to solve some of these problems, in the previous paper [1] we preferred to choose finite-dimension molecular models, employed also in the present case. Starting from the molecular precursor adopted in the on-surface synthesis, then an isolated fragment of the final 2D crystal has been considered together with some complexes of this fragment with Au clusters, in order to model the interaction expected with the Au surface. The Gaussian code has been used to carry out these calculations, employing PBE0 functional combined with cc-pVTZ basis set for C and H and ECP60MDF pseudopotential and VTZ basis set for Au [111].

The interaction with gold is the key point in the on-surface synthesis, as described in detail by Sun and co-workers in the paper reporting the preparation of these systems [2]. This interaction generates also peculiar trends in the Raman spectra, which are discussed in the main text: starting from the isolated precursor, the synthesis is done by annealing through the mediation of the gold surface and an evident downshift is observed in the Raman spectrum in the region above 2000 cm<sup>-1</sup>, where the characteristic bands of the C-C stretching vibrations of the sp carbon domains are found. The trends observed for 2D sp-sp<sup>2</sup> carbon nanonetwork parallel those observed for the 1D polymer [1], revealing that the interaction with the gold surface affects the strength of the sp C-C

bonds, reducing their force constants and hence downshifting the wavenumber of the band associated to C-C stretching normal modes. For the 1D case, this interpretation has been indeed carried out based on DFT calculations of molecular models where the interaction with Au was modeled by the interaction with small Au clusters. Indeed, contrary to experimental results, modeling only the isolated fragment of the final system would predict an upward shift of the Raman  $2000\text{ cm}^{-1}$  band with respect to the precursor, indicating that the interaction with Au is the main responsible for the modulation of the Raman spectra.

The same behaviour is found also for the 2D case, as shown by the DFT computed spectra reported in Figure S3 (all the DFT computed wavenumbers have been scaled by 0.963, see main text for details).



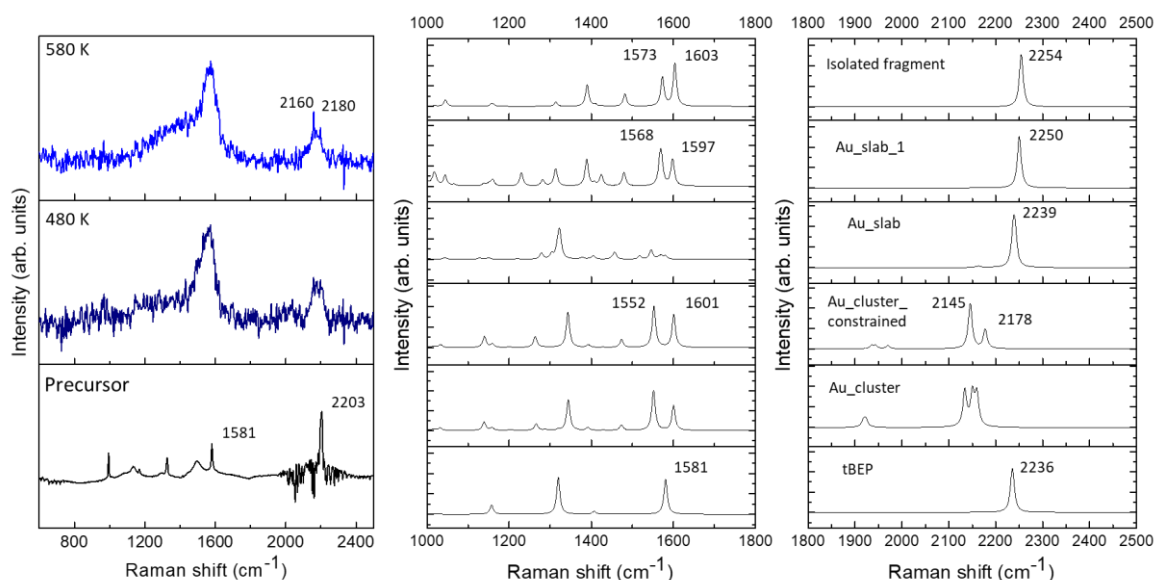
**Figure S3:** DFT computed Raman spectra of the precursor molecule and of molecular models which approach the real 2D sp-sp<sup>2</sup> carbon system on Au(111).

Starting indeed from the tBEP precursor ( $2236\text{ cm}^{-1}$ ), the isolated fragment would present a band at  $2254\text{ cm}^{-1}$ , while for the model where the interaction with Au is modeled by means of Au<sub>4</sub> clusters the shift of the Raman band is in the opposite direction, generating new bands at  $2145\text{ cm}^{-1}$ , in agreement with the experiments.

In figure S4, these spectra are compared with the experimental ones, showing some interesting results:

1. The DFT computed Raman spectrum of the tBEP precursor is in very good agreement with the experimental one, suggesting that the level of theory is adequate for a very accurate description of Raman spectra.
2. Upon annealing (i.e. formation of the final 2D sp-sp<sup>2</sup> carbon system), the sp-carbon stretching band shifts from  $2203\text{ cm}^{-1}$  for the precursor down to  $2180\text{ cm}^{-1}$  and  $2160\text{ cm}^{-1}$ . This downshift can be reproduced only by modelling explicitly the interaction with Au<sub>4</sub> clusters.

3. A downshift is found experimentally also for the phenyl stretching Raman band at  $1581\text{ cm}^{-1}$  for the precursor, that is reproduced by all the DFT calculations. In the calculations, considering also the other models discussed below, a manifold of other bands are present between  $1000$  and  $1400\text{ cm}^{-1}$ . Many of these bands are due to spurious C-H wagging normal modes localized on the phenyl end groups, which are not present in the real system where the connectivity of the phenyl is clearly different.



**Figure S4:** Detailed comparison between experimental and calculated spectra.

Even if the model of the cluster can give a reliable interpretation of the experimental Raman spectra, in this work we tried also to use molecular models which more closely mimick the real extended nanostructure found experimentally by STM.

First, we can notice that the complex with  $\text{Au}_4$  clusters the structure of the fragments presents phenyl end-groups which are largely distorted from planarity, contrary to the planar conformation of the real 2D system. Even if this should not affect significantly C-C stretching modes on the sp carbon domains, a new calculation has been carried out by constraining the fragment geometry to be closer to planarity: as expected the Raman spectrum so obtained predicts again a downshift of the sp carbon stretching Raman bands, in agreement with both experiments and the previous unconstrained model. Therefore, we can rule out any relevant and spurious effect due to the conformation of the end groups on the Raman bands here discussed.

In order then to extend our model, instead of  $\text{Au}_4$  clusters, the interaction with the gold surface has been taken into account by a molecular model where the same fragment is now interacting with a planar and triangular portion of a (111) Au slab formed by 32 Au atoms. The cartesian coordinates of this slab have been fixed, re-optimizing only the relative distances between the fragment and the slab in addition to the intramolecular structure of the fragment. The Raman response, reported in Fig. S3 and S4, has been then computed on the final optimized geometry. Interestingly, in this case, the C-C stretching Raman band of sp C domains is computed at  $2250\text{ cm}^{-1}$ , i.e. at larger frequencies than the precursor ( $2236\text{ cm}^{-1}$ ) and contrary to the experimental findings. The reason for this can be found by analysing the optimizing geometry: while terminal phenyl groups like to interact preferentially with gold atoms, the sp carbon domains have a distance larger than  $3.5\text{ \AA}$  from the surface, indicating that a very weak interaction is found with Au atoms. Therefore, interactions with Au have a negligible effect on the C-C bond properties and

on their vibrations. Indeed, the sp C domains are closer to the case of the isolated fragment, showing computed wavenumber of 2254 cm<sup>-1</sup>.

The inefficiency of this model in describing experiments could be due to the inefficiency of DFT methods in describing Van der Waals interactions, which, in the case of Au<sub>4</sub> clusters, were compensated by the fact that a shorter and more “covalent character” was predicted for the Au-C interaction.

A possible solution for this problem can be found by introducing Grimme’s D3 for dispersion interactions in the slab model: however the computed spectra in this case didn’t show significant differences if D3 corrections are introduced demonstrating that the correct description of the fragment with the Au slab is not related to a more accurate description of intermolecular Van der Waals interactions.

- [1] Rabia, A.; Tumino, F.; Milani, A.; Russo, V.; Li Bassi, A.; Achilli, S.; Fratesi, G.; Onida, G.; Manini, N.; Sun, Q., et al. Scanning tunneling microscopy and Raman spectroscopy of polymeric sp–sp<sup>2</sup> carbon atomic wires synthesized on the Au (111) surface. *Nanoscale* **2019**, *11*, 18191–18200.
- [2] Sun, Q.; Cai, L.; Ma, H.; Yuan, C.; Xu, W. Dehalogenative homocoupling of terminal alkynyl bromides on Au (111): incorporation of acetylenic scaffolding into surface nanostructures. *ACS Nano* **2016**, *10*, 7023–7030.