Impact of screening and relaxation onto weakly coupled 2D heterostructures

T.T. Nhung Nguyen¹, T. Sollfrank¹, and C. Tegenkamp¹∗
¹ Institut für Physik, Technische Universität Chemnitz, Reichenhainer Str. 70, 09126 Chemnitz, Germany
² Department of Mathematics and Physics, University of Stavanger, Norway and
³ Theoretische Materialphysik, Universität Paderborn, D 33098 Paderborn, Germany
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The stacking of different 2D materials provides a promising approach to realize new states of quantum matter. In this combined scanning tunneling microscopy (STM) and density functional theory (DFT) study we show that the structure in weakly bound, purely van der Waals (vdW) interacting systems is strongly influenced by screening and relaxation. We studied in detail the physisorption of lead phthalocyanine (PbPc) molecules on epitaxial monolayer graphene on SiC(0001) as well as on highly ordered pyrolytic graphite (HOPG), resembling truly 2D and anisotropic, semi-infinite 3D supports. Our analysis demonstrates that the different deformation ability of the vdW coupled systems, i.e. their actual thickness and buckling, triggers the molecular morphology and exhibits a proximity coupled band structure. It thus provides important implications for future 2D design concepts.

Heterostructures made layer by layer in a precisely chosen sequence out of 2D materials were suggested to design bulk quantum materials with entirely new functions [1]. Indeed, proximity coupling reveals superconductivity in twisted bilayer graphene [2, 3]. The absence of dangling bonds in 2D materials is expected to allow a flexible and lego-like epitaxial growth of lattice mismatched materials in random order [4].

However, as fabricating a 3D stack out of 2D sheets, the same layers may experience a different coupling, e.g. due to modified screening. Coulomb interaction in 2D and 3D is fundamentally different [5]. In contrast to the isotropic 3D case, for 2D the charge is redistributed on a circle around the point charge, i.e. the residual electric field depends on the polar angle, resulting in a non-local screening behavior which leads usually to strong and k-dependent renormalization of quasiparticle energies, e.g. excitons [6–8] and reduced energy gaps [9–11].

Among thousands of feasible 2D materials [12], graphene is still the most perfect and flexible one, thus ideal to elucidate principles of proximity coupling. Epitaxial graphene on SiC(0001) provides the flexibility to control the interface and its electronic properties [13–15]: monolayer graphene (MLG) grown on SiC(0001) is n-type doped while quasi-free monolayer graphene (QFMLG) on the same substrate is slightly p-type doped [16]. HOPG, in contrast, is charge neutral and represents the semi-infinite 3D counterpart of graphene [17].

Long-ranged ordered molecular 2D structures can be realized also by physisorption of π-conjugated organic molecules on surfaces [18]. Their combination with solid state 2D structures proposes advanced stacking sequences with tailored properties. However, the comprehensive understanding of the physisorption process can become a formidable challenge. Usually, the adsorbate layer and surface lattice are not commensurate. Long-range dispersing forces between the molecules provide a possibility for various phases. The complex interaction scheme with the substrate often comes along with charge transfer (between substrate and adsorbate) superimposing the effect of screening.

Here, the shuttlecock-like lead phthalocyanine (PbPc) molecule with a large gap between the highest occupied and lowest unoccupied molecular orbitals, HOMO and LUMO, helps to suppress charge transfer with the substrate. It thus provides an excellent candidate to study implications of screening and proximity coupling in physisorbed systems. It contains four benzene-pyrrole moieties, which are connected via meso-aza nitrogens. The central Pb atom is coordinated to the four adjacent pyrrole nitrogens and is located outside the molecular plane further reducing the interaction with the substrate.

In this Letter, we analyzed the adsorption of PbPc on variously doped epitaxial graphene and HOPG. For QFMLG and MLG, the buckling of the graphene layer promotes a quasi-free, densely packed and chiral PbPc molecular layer structure with almost identical lattice parameters. Only minor 2D screening is observed, so that the molecular states remain almost unaffected. In contrast, large substrate induced dispersion of the HOMO is found on HOPG, where the more distant molecules interact via the substrate predominantly. Here, π-stacking leads to proximity coupling of PbPc with deeper graphite layers and to a strongly k-dependent reduction of the molecular gap.

As substrates epitaxial monolayer graphene (MLG) and hydrogen-intercalated quasi-free monolayer graphene (QFMLG) on semi-insulating 6H-SiC(0001) as well as highly ordered pyrolytic graphite (HOPG) were used. While HOPG resembles a charge neutral anisotropic 3D
material, MLG and QFMLG are both 2D materials but with completely different electrochemical potentials [17]. Details about fabrication and characterization of the substrates are reported elsewhere [19–22]. The adsorption of PbPc molecules was done at 300 K under ultra high vacuum with same adsorption rates in order to allow a direct comparison [23]. The atomic structure and positions of the PbPc molecule w.r.t. graphene (small inset) are shown in the inset. The parameters are reported in Tab. I.

TABLE I. Lattice parameters from STM and DFT for molecular PbPc layers on HOPG and (QF)MLG as well as for a freestanding PbPc layer. \(b_1\) and \(b_2\) denote the lattice constants as shown in Fig. 1. \(\alpha\), \(\beta\) and \(\gamma\) denote the angles of the unit cell, the rotation of the molecule and the orientation of the unit cell w.r.t. the graphene lattice, respectively. The minimum heights of adsorption \(d\) for atomic type (C/N/Pb) are indicated in Fig. 2, together with the tilting angle \(\vartheta\) of the molecules and the buckling \(\epsilon\) of the topmost C layer. \(N\) denotes the number of C atoms per layer. \(E_{b/C}\), \(E_{b/PbPc}\) and \(E_{b,intra}\) refer to the binding energies per substrate C atom, per molecule and the intra molecular layer contribution.

|                | free layer | MLG        | QFMLG      | HOPG       |
|----------------|------------|------------|------------|------------|
| \(b_1\) (nm)  | 1.42 ± 0.05| 1.40 ± 0.05| 1.58 ± 0.05|            |
| calc.          | 1.35       | 1.37       | 1.54       |            |
| \(b_2\) (nm)  | —          | 1.38 ± 0.05| 1.40 ± 0.05| 1.49 ± 0.05|
| calc.          | 1.33       | 1.30       | 1.54       |            |
| \(\alpha\) (°) | 90.3 ± 1.0  | 90.0 ± 1.0  | 90.1 ± 1.0  |            |
| calc.          | 98.3       | 91.9       | 92.2       |            |
| \(\beta\) (°) | 30 ± 3     | 30 ± 3     | 30 ± 3     |            |
| \(\gamma\) (°)| 39.2 ± 2.0 | 38.5 ± 2.0 | 30.5 ± 2.0 |            |
| calc.          | 39.4       | 39.1       | 30.0       |            |
| height \(d\) (Å) | 2.5/3.5/4.6 | 2.3/3.5/4.7 | 3.1/3.3/4.7 |            |
| buckling \(\epsilon\) (Å) | 0.51 | 0.67 | 0.02 |            |
| tilting \(\vartheta\) (°) | 9.2 | 9.5 | 0.2 |            |
| \(N_{C/layer}\) | 68 | 68 | 90 |            |
| \(E_{b/C}\) (meV) | 29 | 31 | 26 |            |
| \(E_{b/PbPc}\) (eV) | 1.18 | 1.97 | 2.11 | 2.35 |
| \(E_{b,intra}\) (eV) | 1.18 | 0.25 | 0.24 | 0.01 |

Our experiments are supplemented by DFT calculations using a supercell approach and periodic boundary conditions. For HOPG, molecular layers of PbPc molecules were modeled on 6 layer thick Bernal-stacked graphite. Thereby, the simplicity of the substrate allows a direct modeling in the experimentally observed quasi-square surface unit cell (with \(N=90\) atoms per C layer, see Tab. I). In contrast, for QFMLG and MLG, square unit cells are either incommensurable with the underlying SiC(0001) substrate or the graphene layers. As a result, the unit cell of PbPc on (QF)MLG/SiC(0001) contains at least two molecules. However, the absence of any indications in the STM experiment suggests that the SiC part of the substrate plays a minor role. Thus, the MLG calculations were restricted to a simplified unit cell containing one PbPc, where the interaction with the substrate (68 atoms per C layer) is reduced to the topmost graphene layer plus a partially H decorated buffer layer, whereby the level of doping increases almost linearly with the number of in this way \(sp^3\)-coordinated C atoms. The doping level, i.e. the position of the Dirac point \(E_D\) (cf. Fig. 5a), can thus be adjusted via the degree of H decoration. For a 0.4 eV shift determined experimentally [22], about 15 % of the C atoms of the buffer layer have to be covalently bound to the underlaying SiC substrate (cf. Fig. 5b), in fair agreement with experiment [24]. Structural relaxation calculations are performed with the Quantum ESPRESSO package using periodic boundary conditions and a \(3\times3\times1\) \(k\)-point sampling [25, 26]. STM images are simulated based on VASP calculations using
the Tersoff-Hamann approach to analyse the tunneling current [27]. Specifically, we use scalar relativistic norm-conserving pseudopotentials and a plane wave basis set with 90 Ry energy cutoff. For structure relaxation the semi-local PBE functional was used to include many-body effects due to exchange and correlation (XC). Afterwards the B3LYP hybrid functional was used to accurately determine the electronic structure for the PBE relaxed structures. The use of B3LYP copes the DFT-underestimation of the molecular HOMO-LUMO gap (see Ref. 28 and 29 and Table II), and allows a 1:1 comparison of the resulting density of states (DOS) with the experimental STS spectra. In all calculations the D3 dispersion correction was used for a reasonable description of non-local correlation effects [30].

Our experiments and calculations clearly reveal an adsorption of PbPc, where the central Pb atom is pointing upwards on HOPG as well as on epitaxial graphene, as shown in Fig. 1. At least 0.3 eV per molecule (0.72 eV on HOPG) is gained by this preferential adsorption geometry. This is in contrast to Au(111) surfaces, where PbPc molecules show both, up- and down configurations [31]. PbPc on Cu(100) and Ag(100) have been found to form a chiral monolayer structure, while on Pd(100) a stable achiral state was reported [32, 33]. The latter adsorption geometry was explained by stronger hybridization between the pₓ orbital of the macrocyclic C atoms in PbPc and the 4d orbitals of the Pd substrate.

PbPc on all the investigated graphene and graphite templates forms highly-ordered chiral monolayer structures with a single PbPc molecule in quasi-square unit cells, as shown in Fig. 1 exemplarily for QFMLG [23]. Table I summarizes the lattice parameters and molecular orientations which were deduced from STM images taken across the edges of the PbPc islands (cf. with Ref. [23]). They are nicely confirmed and rationalized by our DFT simulations, i.e. by minimizing total energy while varying cell size and shape.

The lattice parameters for PbPc on QFMLG and MLG are similar (even identical in theory), while the parameters found on HOPG are considerably larger by about 10% (cf. Tab. I). The different lattice parameters come along with specific details of the adsorption structure. The characteristic shuttlecock structure of the free PbPc relaxes upon physisorption on all the three substrates. In case of HOPG, the C₄ᵥ symmetry of the gas phase PbPc molecules is retained, but all wings are found almost planar, cf. Fig. 2. It maximizes the attractive vdW interaction per molecule with the graphitic template and resembles the geometry of isolated physisorbed molecules [34–36]. The adsorption height of the C-atoms of about 3.1 Å (cf. Tab. I) is similar to the interlayer distance in graphite. Together with the planar adsorption geometry this suggests π−π* stacking as a predominant driving force. In essence, this stacking gives rise to a proximity-coupled band structure, as we will show below.

In contrast, the C₄ᵥ symmetry of the PbPc upon adsorption on (QF)MLG is lifted. Two neighboring benzene-pyrrole units are bended towards the surface, while the others are lifted to different extent (cf. Fig. 2). The formation of a layer of in this way tilted molecules is in agreement with the asymmetry seen in the STM height profiles taken along two principal axes of the molecules on (QF)MLG (cf. Fig. 3 b,c). Details of the height profiles are shown in the close-up in panel d) and coincide in all cases with profiles obtained from DFT calculated STM images shown in Fig. 4.

The tilted structure on (QF)MLG allows a closer arrangement with strongly increased (× 20) intermolecular coupling, Eₜₜ, intra (see Tab. I) while providing a maximum binding energy per substrate area (i.e. per C-atom). The resulting lattice constants are about 10% smaller than on HOPG and, notably, comparable to a potential free-standing molecular PbPc layer [37].

What is the driving force behind the different adsorption schemes? — The geometry of PbPc on MLG and QFMLG is very similar, despite their different electrochemical potentials. Obviously, the doping level of the two 2D substrates are of minor relevance [17]. According
FIG. 4. Comparison of measured (left) and DFT simulated (right) STM patterns for negative (HOMO, bottom) and positive voltages (LUMO, top), i.e. occupied and empty states. The tunneling conditions, given in (nA/V), were: a) 0.2/+2, b) 0.2/-2, c) 0.2/+2, d) 0.5/-2, e) 0.1/+1.6, f) 0.2/-2, whereby the current was chosen in order to optimize the contrast.

to recent transport measurements [23], charge transfer is also not taking place, in agreement with the present STS and DFT calculations (see below).

A conceivable reason is the corrugation of epitaxial graphene on SiC. The buckling facilitates adsorption of tilted PbPc molecules: The topmost graphene layer is considerably upwards bended towards the PbPc macrocycle compensating the tilting-induced losses in vdW interaction. Although the exfoliation energy for HOPG is one order of magnitude lower than in case of MLG/SiC [38, 39] a local deformation of the uppermost C layer in HOPG costs by far more energy (182 meV instead of 86 meV for MLG). Obviously, the inherent corrugation of epitaxial graphene layers (the lateral strain also responsible for the buckling) allows for a flexible adaptation of the substrate to the adsorbed molecular structures. Thus, the tilting of the PbPc molecule is a direct consequence of the deformation ability of the 2D support.

A common STM feature for all three substrates is a donut-like shape of the occupied state in the center of the molecule. It was seen for all investigated substrates and is nicely reproduced by DFT in Fig. 4 [23]. This demonstrates that the central Pb atom does not contribute to the HOMO (cf. Fig. 2, 5b,c) for all investigated substrates, whereby this spectroscopic fingerprint becomes most obvious at slightly different tunneling voltages, see Fig. 4. For a more detailed analysis, additional STS measurements were performed. In Fig. 5 a) averaged dI/dV-spectra are shown and compared with the B3LYP-D3 calculated density of states (DOS):

(i) While the energies for the HOMO and LUMO states of gas phase PbPc [28] and adsorbed on QFMLG as well as HOPG are similar, the spectrum measured on MLG is shifted to lower energies (by ≈0.4 eV), reflecting the n-type doping of MLG. Whereas the position of the LUMO is obvious also in this case, the identification of the HOMO requires theoretical support: Those C atoms (of the buffer layer) covalently bound to the SiC substrate, introduce additional occupied states partially superimposing the HOMO (see bracket in Fig. 5).

(ii) Interestingly, the different doping levels of MLG and QFMLG play no role. Very similar HOMO and only slightly different LUMO STM signatures suggest that both structures experience an almost identical lateral screening behavior. There are also only minor relative shifts of the HOMO and LUMO levels (cf. Tab. II). This is in line with literature where relevant screening effects onto the molecular electronic structure are restricted to substrate 2D-layer distances clearly below 3 Å [40, 41].

Contrary, for HOPG our B3LYP-D3 band structure calculations reveal a large dispersion of the molecular HOMO (∆E_{disp} ≈ 0.39 eV). The LUMO is affected by much lower extend (cf. Fig. 5 d). Similar to the case of metallic substrates [33, 34], the resulting k-point dependent renormalization of the molecular HOMO-LUMO...
gap can be attributed to $\pi$-stacking of the eight macro-
cyclic C atoms (those bridging two N atoms) with the
substrate C atoms (see Fig. 5 b,c) which is largest for
the second graphite layer. Notably, this hybridization
effect is not coming along with a gap opening in the sub-
strate bands and, thus, mimics an example of proxim-
ity coupling. The concomitant modification of the band
structure is strongly $k$-dependent, and the maximum size
effect is restricted to rather small regions within the Bril-
louin zone (Fig. 5 d), explaining the shoulder observed in
STS slightly below $-1$ V sample bias. The fact, that the
molecular states of PbPc on HOPG reveal a strongly en-
hanced dispersion, although the intermolecular distance
is larger compared to (QF)MLG, underlines the impor-
tance of a substrate mediated interaction.

In summary, we comprehensively studied vdW inter-
acting heterostructures by means of PbPc monolayer
structures on 2D graphene, (QF)MLG, and semi-infinite
3D graphite, HOPG. Albeit the surface structure of all
samples are the same and charge transfer is not taking
place, the molecular layer reveals very different lattice parameters and underwent different relaxation
schemes. Formation of almost identical densely packed
PbPc molecular layers with strongly tilted molecules were
found on both 2D templates, despite their very differ-
ent work functions, showing that lateral Thomas Fermi
screening plays a minor role. Contrary, the interaction
with the upper graphite (HOPG) layers, in particular
the second, favors an almost planar adsorption of PbPc
at the expense of a considerably larger lattice constant.
The dispersing molecular states unambiguously demon-
strate the presence of a substrate mediated interaction
and the band structure exhibits spectral features of prox-
imity coupling. Therefore, the actual thickness of a 3D
stack built from 2D sheets appears to be decisive for the
vdW heteroepitaxy and impacts recent layer by layer de-

### TABLE II

Calculated HOMO-LUMO gap energies (eV,
B3LYP-D3 hybrid functional) for PbPc on various substrates.

| System                  | isolated gap | $\Delta E_{\text{disp}}$ |
|-------------------------|--------------|-------------------------|
| PbPc isolated (LDA,PZ-D3) | 1.32         |                         |
| PbPc isolated (PBE-D3)   | 1.33         |                         |
| PbPc isolated (B3LYP-D3) | 2.01         |                         |
| freestanding PbPc film (MLG) | 2.03/2.00  | 0.03                    |
| freestanding PbPc film (QFMLG) | 2.01/2.00  | 0.01                    |
| freestanding PbPc film (HOPG) | 2.01/2.01  | 0.00                    |
| PbPc/MLG                | 1.98         | 1.98/1.94 0.05          |
| PbPc/QFMLG              | 1.95         | 1.94/1.85 0.09          |
| PbPc/HOPG               | 2.00         | 2.00/1.75 0.39          |

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² christoph.tegenkamp@physik.tu-chemnitz.de
uwegerstmann@upb.de

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