

Impact of screening and relaxation on weakly coupled two-dimensional heterostructuresT. T. Nhung Nguyen, T. Sollfrank, and C. Tegenkamp^{✉*}*Institut für Physik, Technische Universität Chemnitz, Reichenhainer Strasse 70, 09126 Chemnitz, Germany*E. Rauls¹ and U. Gerstmann^{2,†}¹*Department of Mathematics and Physics, University of Stavanger, 4036 Stavanger, Norway*²*Theoretische Materialphysik, Universität Paderborn, D 33098 Paderborn, Germany*

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The stacking of different two-dimensional (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 three-dimensional (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.

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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 legolike 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 nonlocal 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 quasifree 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 shuttlecocklike 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 quasifree, 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 quasifree monolayer graphene

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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. α , β , and γ 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 ϑ of the molecules and the buckling ϵ 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 intramolecular 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	1.37	1.54
b_2 (nm)		1.38 ± 0.05	1.40 ± 0.05	1.49 ± 0.05
Calc.	1.33	1.30	1.30	1.54
α (deg)		90.3 ± 1.0	90.0 ± 1.0	90.1 ± 1.0
Calc.	98.3	91.9	91.9	92.2
β (deg)	–	30 ± 3	30 ± 3	30 ± 3
γ (deg)		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 ϵ (Å)	–	0.51	0.67	0.02
Tilting ϑ (deg)	–	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

(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 [16,19–21]. In all cases, the adsorption of PbPc molecules was done at 300 K under ultrahigh vacuum with identical adsorption rates in order to allow a direct comparison [22]. The atomic structure and positions of molecular energy levels were investigated by low temperature scanning tunneling microscopy (LT-STM, 6 and 80 K). Scanning tunneling spectroscopy (STS) was recorded using a lock-in technique (20 meV, 1 kHz). For the dI/dV spectra an average of at least ten curves were acquired at various positions across the molecules.

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 six-layer-thick Bernal-stacked graphite. Thereby, the simplicity of the substrate allows a direct modeling in the experimentally observed quasisquare surface unit cell (with $N = 90$ atoms per C layer, see Table 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. 5(a)], can thus be adjusted via the degree of H decoration. For a 0.4 eV shift determined experimentally [21], about 15% of the C atoms of the buffer layer have to be covalently bound to the underlying SiC substrate [cf. Fig. 5(b)], in fair agreement with experiment [23].

Structural relaxation calculations are performed with the QUANTUM ESPRESSO package using periodic boundary conditions and a $3 \times 3 \times 1$ k -point sampling [24,25]. STM images are simulated based on VASP calculations using the Tersoff-Hamann approach to analyze the tunneling current [26]. Specifically, we use scalar relativistic norm-conserving pseudopotentials and a plane wave basis set with 90 Ry energy cutoff. For structure relaxation the semilocal 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 copies the DFT underestimation of the molecular HOMO-LUMO gap (see Refs. [27,28] 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 nonlocal correlation effects [29].

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 [30]. 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 [31,32]. The latter adsorption geometry was explained by stronger hybridization between the p_z orbital of the macrocyclic C atoms in PbPc and the $4d$ orbitals of the Pd substrate.

TABLE II. Calculated HOMO-LUMO gap energies (eV, B3LYP-D3 hybrid functional) for PbPc on various substrates. For comparison the values for isolated (single) molecules [also for (semi-)local PBE/LDA functionals] and freestanding molecular monolayers (B3LYP-D3) are also given. For the periodic structures the k -point dependence ($12 \times 12 \times 1$ sampling) is documented by the minimum/maximum values and the dispersion $\Delta E_{\text{disp}} = \text{gap}_{\text{max}} - \text{gap}_{\text{min}}$.

System (XC-funct.)	Isolated	$\text{gap}_{\text{max/min}}$	ΔE_{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

PbPc on all the investigated graphene and graphite templates forms highly ordered *chiral* monolayer structures with a single PbPc molecules in quasisquare unit cells, as shown in Fig. 1 exemplarily for QFMLG [22]. 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. [22]). 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. Table 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 C_{4v} 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 graphene template and resembles the geometry of isolated physisorbed molecules [33–35]. The adsorption height of the C atoms of about 3.1 Å (cf. Table I) is similar to the interlayer distance in graphite. Together with the

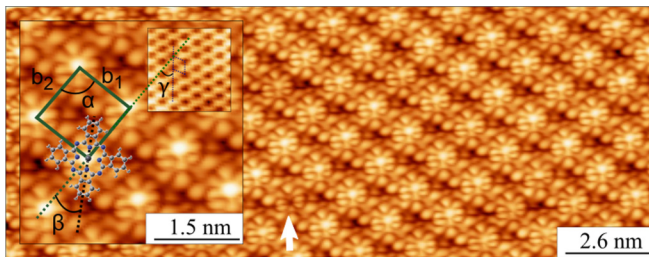


FIG. 1. Large scale STM image of a densely packed molecular layer of PbPc on QFMLG (0.2 nA, +2 V). The imperfection (marked by an arrow) is most likely a Pc molecule with a missing Pb atom. The unit cell and relative orientation of the PbPc molecule w.r.t. graphene (small inset) are shown in the inset. The parameters are reported in Table I.

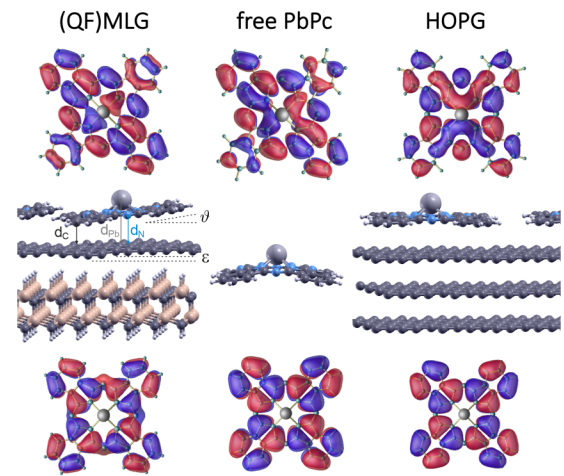


FIG. 2. Structure of PbPc monolayers on (QF)MLG (tilting angle ϑ) and HOPG, in comparison with isolated (free) PbPc molecules. The molecular HOMOs (bottom) and LUMOs (top) for the molecular species alone are also shown. For HOPG, the strong coupling to the other layers prevents the topmost layer from corrugation and buckling ϵ , cf. Table I.

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 C_{4v} 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 a 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 the orthogonal axes with strongest intensity anisotropies of the molecules on (QF)MLG [cf. Figs. 3(b) and 3(c)]. Details of the height profiles are shown in the closeup in Fig. 3(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 ($\times 20$) intermolecular coupling, $E_{b,\text{intra}}$ (see Table 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 freestanding molecular PbPc layer [36].

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 to recent transport measurements [22], 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, more precisely the flexibility of the C atoms to change their z coordinates, facilitates adsorption of *tilted* PbPc molecules: The topmost graphene layer is partially upwards bended towards the PbPc macrocycle compensating for the tilting-induced losses in vdW interaction. Although the exfoliation energy for MLG/SiC is one

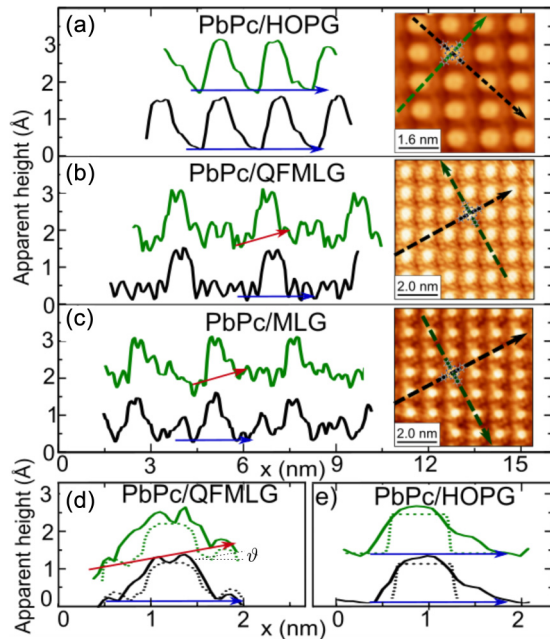


FIG. 3. High resolution STM images of PbPc monolayers on (a) HOPG (0.2 nA, -2 V), (b) QFMLG (0.2 nA, -2 V), and (c) MLG (0.2 nA, -1 V) and corresponding height profiles taken along two main molecular axes as indicated. A tilting (red arrows) is seen only on (QF)MLG along one direction (green). (d) and (e) Magnifications of PbPc/QFMLG and PbPc/HOPG, respectively, together with profiles (dotted lines) obtained from DFT calculated STM images, Fig. 4.

order of magnitude higher than in the case of HOPG [37,38] a local deformation of the topmost graphene layer on SiC costs by far less energy (86 meV instead of 182 meV for MLG). Obviously the inherent corrugation of epitaxial graphene layers (the lateral strain also responsible for the buckling) allows for a flexible adaption of the substrate to the adsorbed molecu-

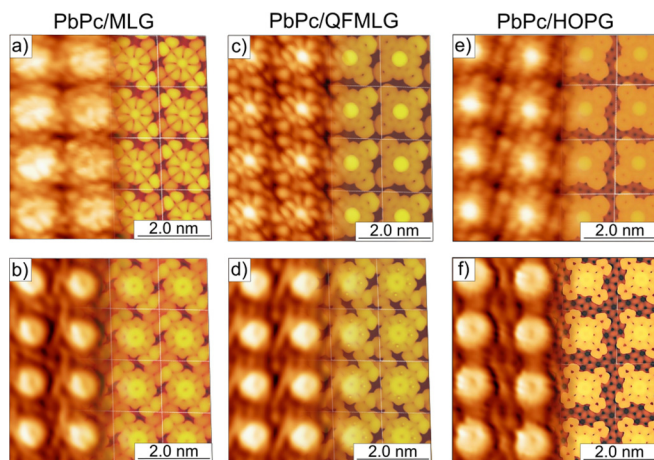


FIG. 4. Comparison of measured (left) and DFT simulated (right) STM patterns for negative (HOMO, bottom) and positive voltages (LUMO, top), i.e., occupied and empty states. The tunneling conditions, given in (nA/V), were: (a) 0.2/ + 2, (b) 0.2/ -2 , (c) 0.2/ + 2, (d) 0.5/ -2 , (e) 0.1/ + 1.6, and (f) 0.2/ -2 , whereby the current was chosen in order to optimize the contrast.

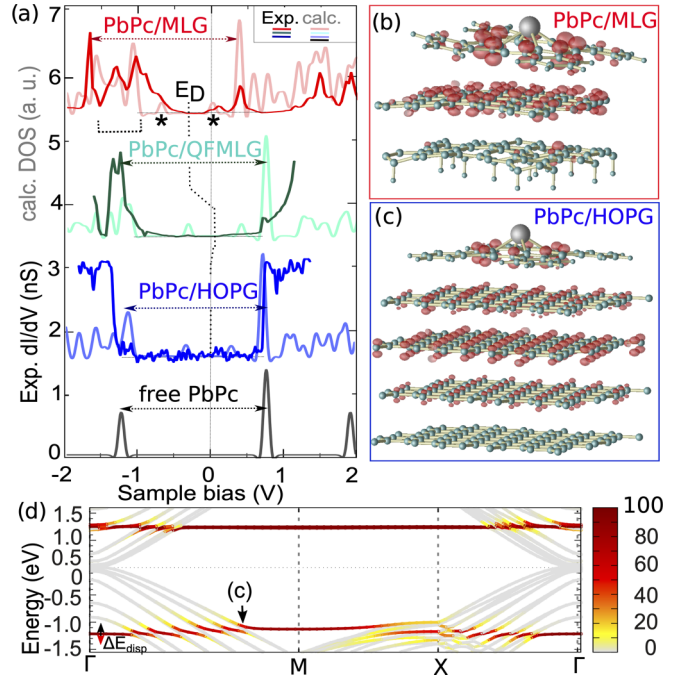


FIG. 5. (a) Averaged dI/dV spectra (set point: 0.2 nA, -1 V) taken for PbPc on MLG, QFMLG, and HOPG compared with calculated DOS (B3LYP-D3, shifted $3 \times 3 \times 3$ k sampling). Structure and molecular HOMO interacting with the substrate for MLG (b) and HOPG (c), whereby the spatial distribution of the HOMO (red) is exemplarily shown for a k point indicated by the arrow in (d): For HOPG, the k -dependent contributions of the molecule (in percent) to the HOMO and LUMO are indicated by the color scale (d). The π states of the substrates are labeled by (*). Due to finite k sampling, they appear at finite energies (centered around the Dirac point E_D) and allow the accurate determination of E_D .

lar 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 donutlike 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 [22]. This demonstrates that the central Pb atom does not contribute to the HOMO [cf. Figs. 2, 5(b), and 5(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 [27] 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. Table 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 [39,40].

Contrary, for HOPG our B3LYP-D3 band structure calculations reveal a large dispersion of the molecular HOMO ($\Delta E_{\text{disp}} \approx 0.39$ eV). The LUMO is affected by a much lower extent [cf. Fig. 5(d)]. Similar to the case of metallic substrates [32,33], the resulting k -point dependent renormalization of the molecular HOMO-LUMO gap can be attributed to π stacking of the eight macrocyclic C atoms (those bridging two N atoms) with the substrate C atoms [see Figs. 5(b) and 5(c)] which is largest for the second graphite layer. Notably, this hybridization effect is not coming along with a gap opening in the substrate bands and, thus, mimics an example of proximity 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 Brillouin zone [Fig. 5(d)], explaining the shoulder observed in STS slightly below the -1 V sample bias. The fact that the molecular states of PbPc on HOPG reveal a strongly enhanced dispersion, although the intermolecular distance is larger compared to (QF)MLG, underlines the importance of a substrate mediated interaction.

In summary, we comprehensively studied vdW interacting heterostructures by means of PbPc monolayer structures on 2D graphene (QF)MLG, and semi-infinite 3D graphite HOPG. Albeit the surface structure of all templates 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 different 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 demonstrate the presence of a substrate mediated interaction and the band structure exhibits spectral features of proximity 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 design concepts [1,4].

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