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Influence of intermolecular interactions on the structure of phthalocyanine layers in molecular thin film heterostructures

S. Yim, S. Heutz, and T. S. Jones*

Centre for Electronic Materials and Devices, Department of Chemistry, Imperial College London, SW7 2AZ, United Kingdom

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Free-base phthalocyanine (H_2Pc) molecules have been shown to stack layer by layer when deposited on a plane perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) layer, a structure very different from the α-herringbone structure formed in the bulk or when H_2Pc is deposited at room temperature on noninteracting substrates such as glass. In this paper theoretical studies have been carried out to rationalize this structural modification using van der Waals intermolecular interaction energy calculations. In the case of bulk H_2Pc unit cells, the α-herringbone structure is more stable (by ~6%) than the planar layered structure, consistent with the existence of the α-herringbone structure when H_2Pc is grown on noninteracting substrates. For H_2Pc unit cells on a PTCDA layer, however, the planar layered structure is more stable (by ~9%) in agreement with the experimental observations of a modified H_2Pc structure due to templating. At the energy minimum, the interplanar stacking distance of the planar layered H_2Pc is calculated to be 3.29 Å, in good agreement with the experimentally determined value of 3.33 Å. The calculations indicate that the structural modification in the double layer heterostructure is due to the strong intermolecular interactions between the two layers at the heterointerface.

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I. INTRODUCTION

The controlled growth of molecular thin-film heterostructures is of considerable importance because they form the basis of a wide range of electronic and optoelectronic devices.[1] The properties of these heterostructures depend strongly on the structural quality of the films and the nature of the interface formed between layers of different materials. Organic molecules are bonded to each other by relatively weak van der Waals (vdW) forces and form molecular crystals whose structure is determined by the optimization of intermolecular interactions. The interfacial interaction with other organic crystals, or with relatively inert substrates, is also likely to be of the vdW variety, and highly crystalline structures can be formed without any requirement for lattice matching between dissimilar materials at the interface.[1,2]

Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and free-base phthalocyanine (H_2Pc) are two examples of the types of molecules commonly used in device applications such as light-emitting diodes and photovoltaics.[1] They have also been studied extensively as model systems for the growth and ordering of molecular thin-film materials.[1–3] PTCDA [Fig. 1(a)] has been the archetypal molecular semiconductor for more than a decade. It belongs to the $P2_1/c$ space group and adopts a herringbone structure where the molecules lie in the (102) plane, forming an angle of 42° between their long axes.[4,5] The (102) plane is usually parallel to the substrate for room-temperature deposition.[6,7] H_2Pc [Fig. 1(b)] films have been found to exist as two polymorphs (α and β) when deposited on weakly interacting substrates, both characterized by a herringbone structure with the molecules stacked along the b axis.[8] The α phase is generally obtained by growth at room temperature, whereas high-temperature growth, or postgrowth annealing, leads to the formation of β films, which can be differentiated from the α phase by their structure, surface morphology, and electronic properties.[9–12] The α- and β-phase H_2Pc polymorphs are both monoclinic and belong to the $C2/c$ and $P2_1/a$ space groups, respectively.[13,14] Our recent studies have shown evidence for structural and morphological templating when the different polymorphs of H_2Pc are deposited on top of each other in a bilayer thin-film structure.[15]

The formation of organic thin-film heterostructures can lead to major changes in the properties of a molecular film because the underlying molecular layer (a different material) can exert a strong influence on the growth and structure of the subsequent layer.[16–20] For example, studies of ultrathin bilayers of copper phthalocyanine (CuPc) and PTCDA deposited on Cu(100) showed that the PTCDA monolayers grown on CuPc adopted a structure with a lattice parameter very different to that normally obtained on weakly interacting substrates.[16] It was concluded that the CuPc layer controls the architecture of the subsequent PTCDA layers. The properties of nickel phthalocyanine (NiPc)-PTCDA and vanadyl phthalocyanine (VOPc)-PTCDA double layers have also been studied using optical-absorption spectroscopy and x-ray diffraction (XRD). When PTCDA was grown on NiPc,[17] only the NiPc diffraction peak was present for deposition at 35 °C with the PTCDA diffraction peaks only appearing at 60 °C. It was suggested that these peaks correspond to orientations of the PTCDA layer that are different from a single PTCDA film. When the deposition order was reversed, more severe structural changes were apparent and no diffraction peaks were observed. When the VOPc-PTCDA system was examined,[18] significant perturbations from the single layer properties were also observed, and VOPc crystallized as a different polymorph when deposited on PTCDA.

In a recent study we have shown that a structural templating effect occurs in molecular multilayers based on H_2Pc and

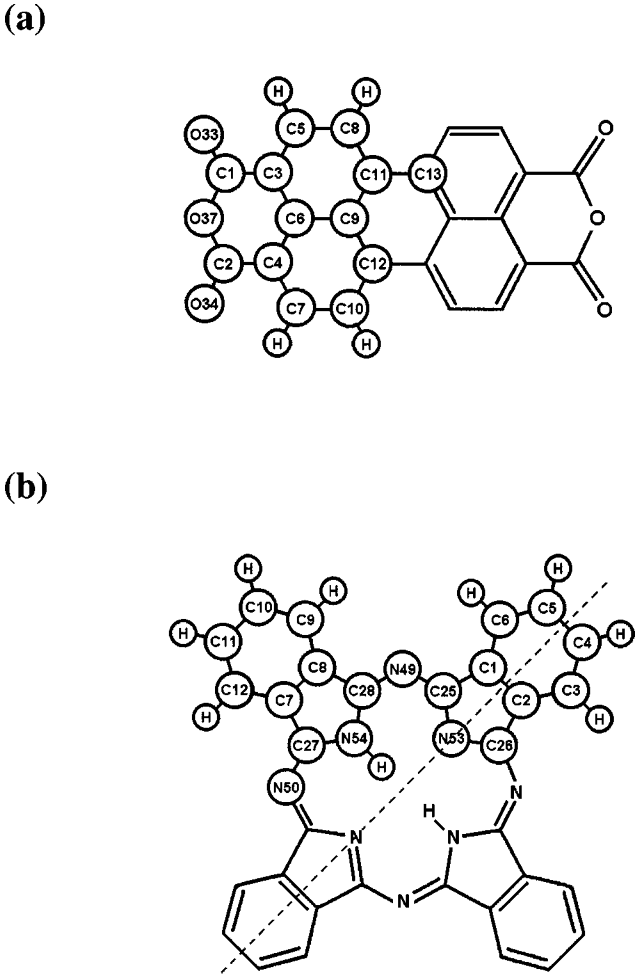

FIG. 1. Molecular structure of (a) PTCDA and (b) H_2Pc. The dashed line in (b) represents the molecular axis defined in the text.

PTCDA.[19,20] The templating effect is most apparent when H_2Pc molecules are deposited on top of an initial planar PTCDA layer. A H_2Pc single layer grown on glass substrates has an α-phase herringbone structure where individual molecular planes are aligned almost perpendicular to the substrates [Fig. 2(a)]. By contrast, a H_2Pc layer deposited onto PTCDA was found to have a planar layered structure with an interplanar stacking distance (determined by XRD) of 3.33 Å [Fig. 2(b)]. From an energetic perspective, the structural modification of the top H_2Pc layer must be a consequence of the optimization of the intermolecular interactions at the heterointerface.

There have been very few theoretical attempts to predict the structure of thin films based on these types of molecules. One study has been reported for CuPc layers deposited on H-passivated Si(001) surfaces.[21] The interactive forces were considered to be of nonbonding character and the structure expected from the vdW interaction energy calculation was in good agreement with experimental frictional force microscopy images. In this paper, we report the results of theoretical calculations of the H_2Pc/PTCDA heterostructure. Calculations are carried out that compare the intermolecular interaction energies of an α-herringbone H_2Pc structure and a planar layered structure of H_2Pc when they are crystallized in the bulk and when deposited on top of an initial PTCDA layer. The calculations provide a very good quantitative explanation for the structural templating effect and the subsequent modification of the H_2Pc thin film in the double layer heterostructure.

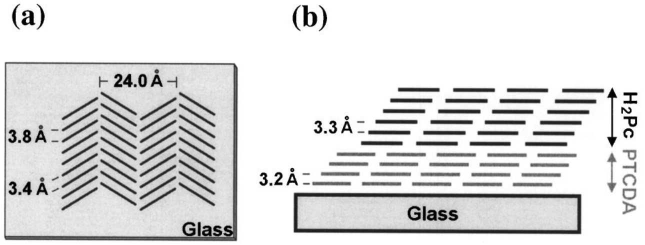

FIG. 2. (a) Molecular arrangement in α-H_2Pc crystals deposited on glass substrates, and (b) a schematic of the layered H_2Pc structure formed when deposited on top of a PTCDA first layer (from Ref. 20).

II. THEORETICAL DETAILS

Three methods have been used for the calculation of the nonbonded vdW interaction energy; the Lennard-Jones 9-6 form, the Lennard-Jones 12-6 form, and the Exp-6 form.[22] The intermolecular interaction energy calculations in this work were performed using a Lennard-Jones (LJ) 9-6 vdW interaction energy for all possible, nonbonded atom pairs, i.e.,

$$E_{\mathrm{vdW(LJ\ 9\text{-}6)}}=\Sigma\varepsilon_{ij}\{2(R_{ij}^{*}/R_{ij})^{9}-3(R_{ij}^{*}/R_{ij})^{6}\}, \qquad (1)$$

where R_{ij} is the distance between the ith and jth atoms, R_{ij}^* is the minimum-energy separation between atoms i and j, and $-\varepsilon_{ij}$ is the energy for the i, j interaction attained at $R_{ij}=R_{ij}^*$. Table I lists the molecular mechanics (MM) force field parameters for the Lennard-Jones 9-6 intermolecular interaction for the individual atoms in PTCDA [Fig. 1(a)] and H_2Pc [Fig. 1(b)]. The arithmetic mean of R_{ii}^* and R_{jj}^*, and the geometric mean of ε_{ii} and ε_{jj} were used to express R_{ij}^* and ε_{ij}, the parameter values between the different types of atoms, i and j. Atom pairs whose distances are greater than 10 Å are neglected in the calculation. It is assumed that there

TABLE I. MM 2X atom types and vdW parameters used in the calculations (see Ref. 22).

Atom		Atom type	R^* (Å)	ε (eV)
PTCDA	H_2Pc			
C1		3	3.60	0.005 20
C3	C1	37	4.00	0.003 47
	C25	57	4.00	0.003 47
	N49	38	3.60	0.006 94
	N53	39	3.60	0.006 94
H	H(-C)	5	2.80	0.001 74
	H(-N)	23	1.60	0.000 87
O33		7	3.20	0.008 67
O37		6	3.30	0.007 81

TABLE II. Structural parameters of H_2Pc and PTCDA obtained from *ab initio*/DFT calculations. Bond lengths are in Å and angles in degrees.

H_2Pc^a		$PTCDA^b$	
C1-C2	1.404	C1-C3	1.478
C2-C3	1.393	C3-C5	1.382
C3-C4	1.397	C3-C6	1.414
C4-C5	1.405	C5-C8	1.399
C1-C25	1.467	C6-C9	1.430
C25-N53	1.365	C8-C11	1.397
C25-N49	1.336	C9-C11	1.433
C28-N49	1.318	C11-C13	1.473
C7-C8	1.414	C1-O33	1.219
C8-C9	1.397	C1-O37	1.389
C9-C10	1.392	C5-H	1.082
C10-C11	1.410	C8-H	1.081
C7-C27	1.453		
C27-N54	1.378		
C27-N50	1.318		
C-H_{av}	1.086		
N54-H	1.014		
C1-C2-C3	121.2	C1-C3-C6	121.1
C2-C3-C4	117.7	C1-O37-C2	125.2
C3-C4-C5	121.1	C3-C1-O37	116.8
C1-C2-C26	105.6	C3-C5-C8	120.7
C2-C26-N53	110.9	C3-C6-C4	119.0
C25-N53-C26	106.9	C3-C6-C9	120.5
N53-C26-N51	127.7	C5-C3-C6	119.6
N49-C25-N53	127.6	C5-C8-C11	121.7
C25-N49-C28	123.7	C6-C9-C11	118.7
C7-C8-C9	120.9	C8-C11-C9	118.8
C8-C9-C10	117.7	C9-C11-C13	118.7
C9-C10-C11	121.2	C11-C9-C12	122.5
C7-C8-C28	107.5	O33-C1-O37	118.7
C8-C28-N54	106.1	H-C5-C3	118.5
C27-N54-C28	112.5	H-C8-C11	120.5
N54-C27-N50	128.2		
N49-C28-N54	128.2		
C28-N54-H	123.7		

[a] Reference 25.

[b] Reference 24.

is no significant contribution to the intermolecular interaction energy from Coulombic forces and higher-order multipoles, since previous calculations for nonpolar molecules have shown this assumption to be generally valid.[21,23]

PTCDA (Ref. 24) and H_2Pc (Ref. 25) molecular structural parameter values (bond lengths and angles), obtained from *ab initio* methods and density-functional theory (DFT) calculations, are listed in Table II. These values are consistent with experimental XRD results[4,26] and previous theoretical calculations.[27] Based on these molecular structures, we have calculated the intermolecular interaction energies of four different H_2Pc unit-cell models: (i) the bulk α-herringbone structure, (ii) a planar layered bulk structure, (iii) the α-herringbone structure on PTCDA, and (iv) a planar layered structure on PTCDA.

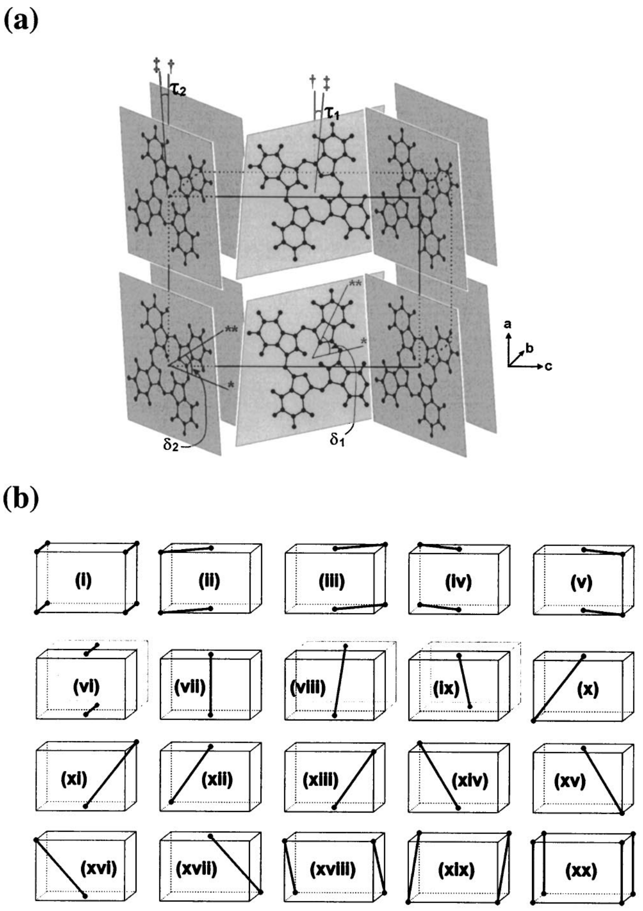

FIG. 3. (a) Structural model and (b) possible molecule pairs for the bulk H_2Pc α-herringbone unit cell. τ_1 and τ_2 are angles between †, the direction normal to the *b*-*c* plane and ‡, the direction of the molecular plane. δ_1 and δ_2 are the angles between *, the intersection of the molecular plane and the *b*-*c* plane, and **, the molecular axis defined in the text.

III. RESULTS AND DISCUSSIONS

A. Bulk H_2Pc unit cells

A schematic model for the α-herringbone H_2Pc unit cell is shown in Fig. 3(a). It consists of two molecules, two center molecules with a weight of $\frac{1}{2}$ and eight corner molecules with a weight of $\frac{1}{8}$. The intermolecular interaction energy of this unit cell was calculated by varying four parameters; τ_1, τ_2, δ_1, and δ_2. The tilt angles of the molecular plane with respect to the direction normal to the unit-cell *b*-*c* plane, τ_1 and τ_2 for the center and corner molecules, respectively, were varied from 0° to 15° with an increment of 0.1°. We define a molecular axis through the two nonhydrogenated pyrrole nitrogens [dashed line in Fig. 1(b)]. The angle between this direction and the intersection of the molecular plane and the unit-cell *b*-*c* plane is then defined as δ_1 and δ_2 for the center and corner molecules, respectively. In the calculation, δ_1 and δ_2 were varied from 0° to 180° with an increment of 0.1°. The fixed unit-cell lattice-parameter values[28] used for the calculation were $a/2 = 13.07$, $b = 3.814$, and $c = 23.97$ Å, and $\beta = 91.1°$. At specific parameter values, the intermolecular interaction energy of the unit cell is the sum of the Lennard-Jones vdW energies for all possible atom pairs. For the α-herringbone H_2Pc unit cell, the number of possible molecule pair types is 20 as shown in Fig. 3(b). The hexadrons in the figure represent the unit cells, and the filled circles and thick lines are molecular centers and molecule pairs, respectively. Some molecule pairs are equivalent; for example, in Fig. 3(b)(i), there are four equivalent molecule pairs, each having a weight factor of $\frac{1}{4}$ since a pair simultaneously belongs to other three unit cells. For the calculation, therefore, these four equivalent molecule pairs were regarded as one molecule pair. For each molecule pair, the number of possible atom pairs is 3364 (58×58) since one H_2Pc molecule contains 58 atoms, therefore, 67 280 (20×3364) atom pairs should be taken into account for calculation of the total energy of the unit cell. At certain parameter values, therefore, the total intermolecular interaction energy of the α-herringbone H_2Pc unit cell is the sum of the Lennard-Jones vdW energies of these 67 280 atom pairs.

The α-herringbone H_2Pc unit cell has a minimum energy of -5.894 eV at $\tau_1 = \tau_2 = 8.6°$, $\delta_1 = 60.4°$, and $\delta_2 = 29.6°$. The energy per molecule corresponds to -2.947 eV since the unit cell consists of two molecules. The vdW interaction energy surfaces for the α-herringbone unit cell of H_2Pc are shown in Fig. 4. Figure 4(a) shows the energy surface drawn with respect to the molecular plane tilt angles, τ_1 and τ_2, when the in-plane molecular rotational angles, δ_1 and δ_2, are fixed at 60.4° and 29.6°, respectively, and Fig. 4(b) shows the energy surface drawn with respect to δ_1 and δ_2 with $\tau_1 = \tau_2 = 8.6°$. The intermolecular interaction energy of the H_2Pc molecules in the α-herringbone unit cell can be divided into two types; (i) the interaction energy between molecules with the same height ($E_{\leftrightarrow}$), and (ii) the interaction energy with molecules positioned on the upper or lower layers ($E_{\updownarrow}$). In Fig. 3(b), the sum of the interaction energy for molecule pairs from (i) to (vi) corresponds to $E_{\leftrightarrow}$, and that from (vii) to (xx) corresponds to $E_{\updownarrow}$. For the α-herringbone unit cell, $E_{\leftrightarrow}$ is -2.471 and $E_{\updownarrow}$ is -0.476 eV at the total-energy minimum.

A schematic model for the planar layered H_2Pc unit cell is shown in Fig. 5(a). The unit cell contains one molecule, with each molecule at the corner of the unit cell contributing a weight of $\frac{1}{8}$. The intermolecular interaction energy of the unit cell was calculated by varying x, y, and z. The lateral displacement parameters (x,y) of a molecule in the upper two-dimensional (2D) quadrate with respect to the corresponding molecule in the lower quadrate were varied from -7 to 7 Å with an increment of 0.1 Å. The interplanar stacking distance between two layers, z, was varied from 0 to 8 Å with an increment of 0.01 Å. We have recently reported that a 2D quadratic H_2Pc unit cell has its minimum intermolecular interaction energy at the lattice parameters, a and b, of 13.97 Å, and a molecular rotational angle in a plane, δ, of 27.4°.[29] These fixed 2D quadrate parameter values were used for the calculation. For the planar layered H_2Pc unit cell, the number of possible molecule pair types is 13 as shown in the Fig. 5(b). The 43 732 ($13 \times 58 \times 58$) atom pairs, therefore, were taken into account for the calculation.

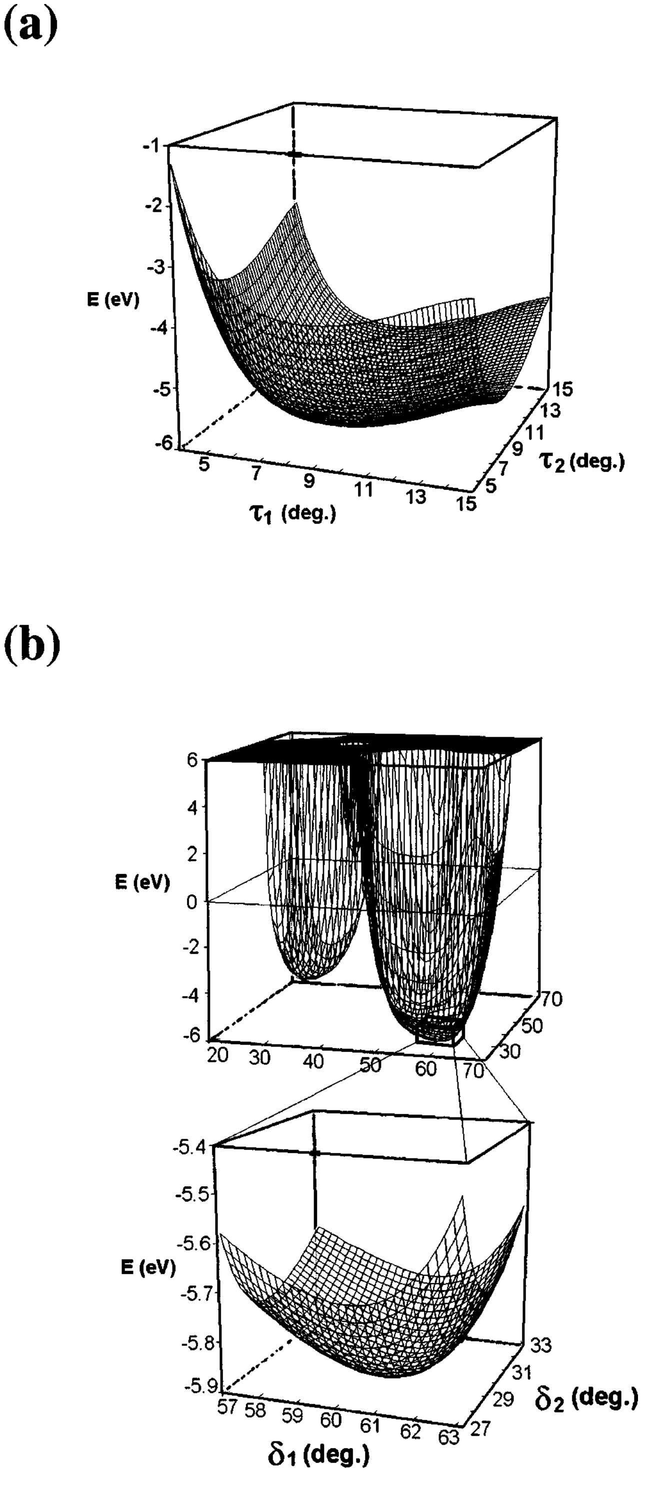

FIG. 4. Intermolecular interaction energy surface diagrams for the bulk α-herringbone H_2Pc unit cell as a function of (a) τ_1 and τ_2 at $\delta_1 = 60.4°$ and $\delta_2 = 29.6°$, and (b) δ_1 and δ_2 at $\tau_1 = \tau_2 = 8.6°$. The lower-energy surface is an expansion around the energy minimum.

The planar layered H_2Pc unit cell has degenerate energy minima of -2.786 eV at $x = \pm 3.4$, $y = \pm 1.0$, and $z = 3.29$ Å, which correspond to the minimum energy per

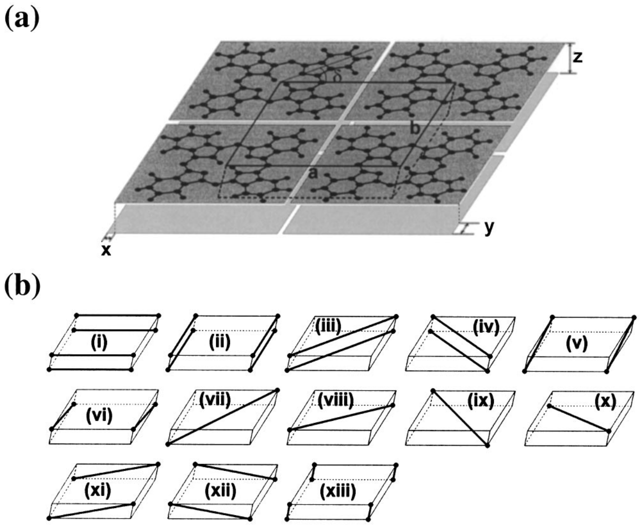

FIG. 5. (a) Structural model and (b) possible molecule pairs for the bulk H_2Pc planar layered unit cell.

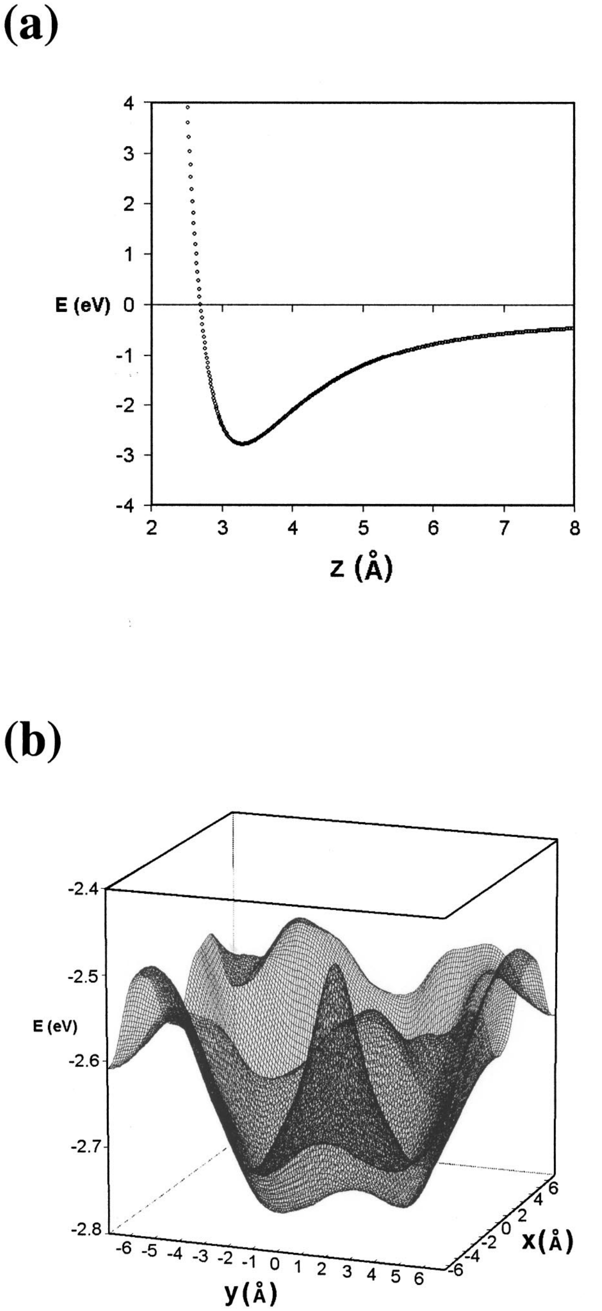

FIG. 6. Intermolecular interaction energies for the bulk planar layered H_2Pc unit cell: (a) energy curve plotted as a function of interplanar stacking distance, z, at $x = 3.4$ and $y = 1.0$ Å, and (b) energy surface drawn as a function of the parallel displacements, x and y, at $z = 3.29$ Å.

molecule since the unit cell consists of one molecule. The vdW interaction energy curves for the planar layered unit cell of H_2Pc are shown in Fig. 6. Figure 6(a) shows the energy curve plotted with respect to the interplanar distance between two 2D quadrates, z. The parallel displacement parameters, x and y, are fixed at 3.4 and 1.0 Å, respectively. Figure 6(b) shows the energy surface drawn with respect to x and y with z fixed at 3.29 Å. This interplanar spacing at the minimum energy corresponds to the experimental value of 3.33 Å obtained for planar layered H_2Pc films deposited on an initial PTCDA layer.[19,20] At the energy minimum for the molecule in a planar layered H_2Pc unit cell, the interaction energy between the molecules within the layer $E_{\leftrightarrow}$ is -0.374 eV and the interaction energy with molecules in different layers $E_{\updownarrow}$ is -2.412 eV.

Coulombic potentials for both α-herringbone and planar layered H_2Pc unit cells were also calculated for the same variable parameter regions. Partial atomic charges for the H_2Pc molecule obtained from DFT calculations[25] were used for these calculations. The intermolecular interaction energies caused by these electrostatic interactions have a negligible effect on the energy minima and the structure determination. For example, in the case of the α-herringbone H_2Pc unit cell, the total interaction energy minimum including the Coulombic potential is -2.839 eV per molecule at $\tau_1 = 8.6°$, $\tau_2 = 8.1°$, $\delta_1 = 60.7°$, and $\delta_2 = 28.7°$, while for the planar layered unit cell, it is -2.752 eV per molecule at $x = \pm 3.0$, $y = \pm 1.4$, and $z = 3.29$ Å. The energy difference between the two structures is 0.187 eV, a value slightly larger than the energy difference obtained after excluding the Coulombic potential (0.161 eV).

B. H_2Pc unit cells on a PTCDA layer

Figure 7 shows schematic models for the α-herringbone [Fig. 7(a)] and planar layered [Fig. 7(b)] H_2Pc unit cells on a PTCDA layer. For the calculations, the lattice parameters of the underlying 2D PTCDA layer consisting of 26 molecules were obtained from electron-diffraction and XRD studies.[5] The intermolecular interaction energies between the H_2Pc unit cell and the underlying PTCDA layer $E_{\updownarrow}$ were calculated with respect to the stacking distance between the H_2Pc unit cell and the PTCDA layer z. At each point of z, the energy was determined by assuming that the H_2Pc unit cell can be placed arbitrarily on the PTCDA layer since the exact position of the H_2Pc unit cell is unknown. This assumption is generally valid since organic molecules such as H_2Pc and

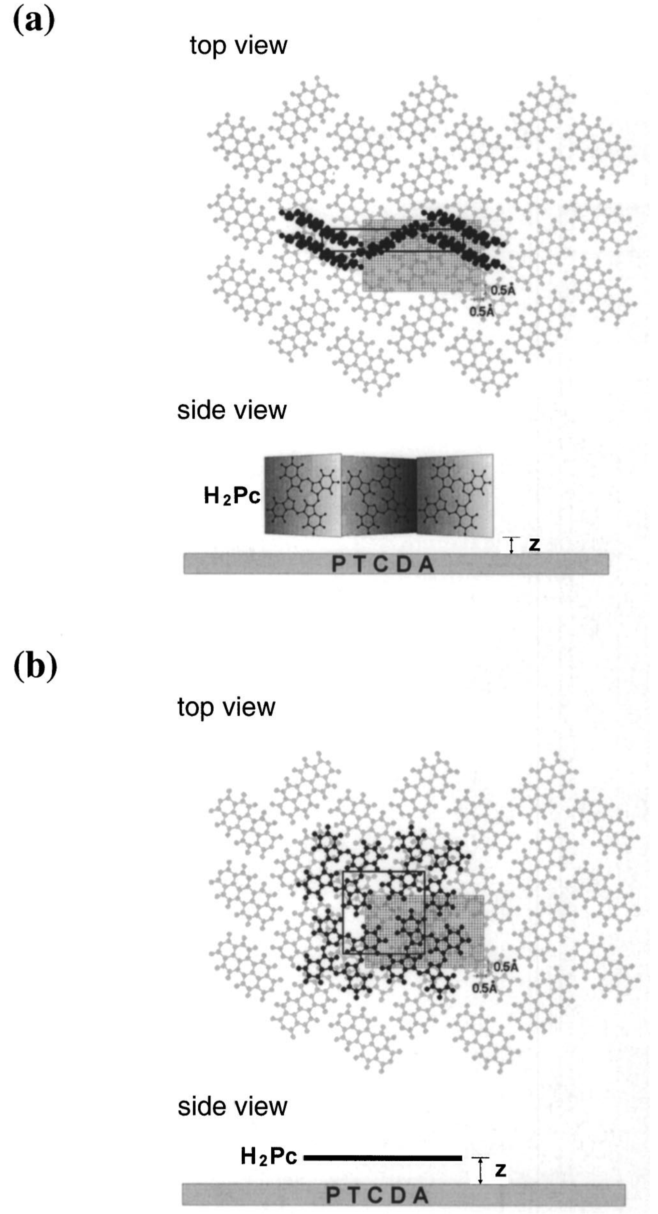

FIG. 7. Schematic models for (a) the α-herringbone H_2Pc unit cell on a PTCDA layer, and (b) the planar layered H_2Pc unit cell on a PTCDA layer. z represents the stacking distance between the H_2Pc unit cell and the PTCDA layer. The black rectangle in (a) and square in (b) represent the H_2Pc unit cells. The PTCDA unit cells (gray rectangle) are divided into 960 square meshes with a length and width of 0.5 Å.

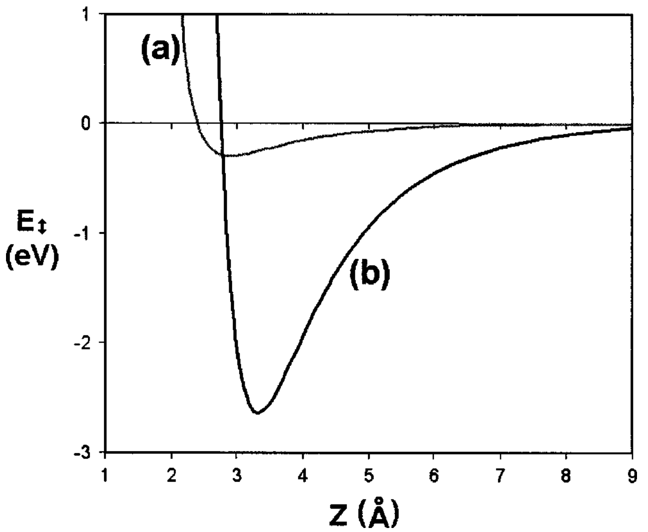

FIG. 8. Intermolecular interaction energy curves between the PTCDA layer and (a) the α-herringbone H_2Pc unit cell and (b) the planar layered H_2Pc unit cell as a function of the stacking distance z.

PTCDA are bonded to each other by relatively weak vdW forces and their lattice-parameter values are quite large, consequently the interfacial interaction between the two different materials does not require any lattice matching. The interfacial interaction energy of a H_2Pc/PTCDA heterostructure depends primarily on the stacking distance between the two layers, with relatively little influence from the lateral displacement. To calculate the intermolecular interaction energy between the arbitrarily positioned H_2Pc unit cell and the PTCDA layer, the underlying PTCDA unit cell (gray rectangle in the figure) was divided into 960 (40×24) square meshes with a length and width of 0.5 Å. At a certain stacking distance z, the interaction energies were then calculated when the center of the H_2Pc unit cell (black rectangle or square in the figure) was positioned on each mesh point, and average values were taken. Once the stacking distance z was determined, any fluctuation of the interaction energy due to a change in lateral displacement was found to be insignificant. The other fixed parameters, τ_1, τ_2, δ_1, and δ_2 for the α-herringbone H_2Pc unit cell, and a, b, and δ for the planar layered H_2Pc unit cell, obtained from the intermolecular interaction energy calculations of bulk H_2Pc unit cells (Sec. III A), were also used for the calculation. In both cases, therefore, the intermolecular interaction energy between the molecules within the layer, $E_{\leftrightarrow}$, is retained.

Figure 8 shows the energy curves between the H_2Pc unit cell and the PTCDA layer $E_{\updownarrow}$, with respect to the stacking distance z. In the case of the α-herringbone structure [Fig. 8(a)], the energy minimum is -0.299 eV at $z = 2.89$ Å, while for the planar layered structure [Fig. 8(b)], it is -2.640 eV at $z = 3.32$ Å. For a given z, any parallel displacement has a minor effect on the energy variation. For example, in the case of the α-herringbone H_2Pc unit cell on PTCDA at $z = 2.89$ Å, the variation in $E_{\updownarrow}$ for any point within the underlying PTCDA unit cell (gray rectangle) is 0.083 eV, from -0.344 to -0.261 eV, and for the planar layered unit cell at $z = 3.32$ Å, it is 0.130 eV, from -2.683 to -2.553 eV. This small variation is also consistent with our assumption that the interaction energy between the H_2Pc unit cell and the PTCDA layer at a specific z can be regarded as an average value irrespective of their exact position.

The energy levels for the four H_2Pc unit-cell structures are shown in Fig. 9. The two in the left box, Figs. 9(a) and 9(b), represent the energy levels for bulk H_2Pc unit cells and the two in the right box, Figs. 9(c) and 9(d), correspond to the H_2Pc unit cells on a PTCDA layer. The energy levels for

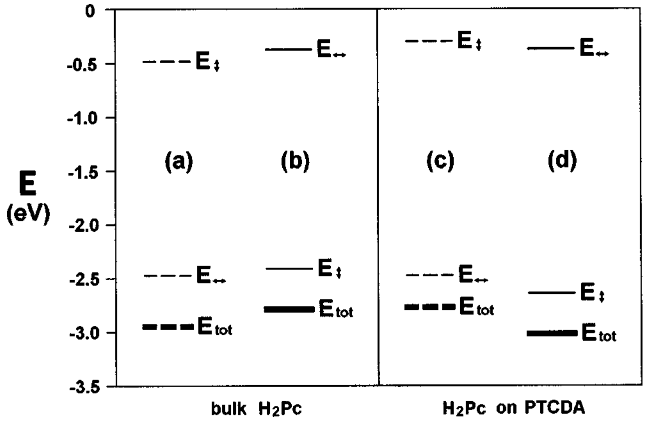

FIG. 9. Energy-level diagrams for four different H_2Pc unit-cell models; (a) the bulk α-herringbone structure, (b) the bulk planar layered structure, (c) the α-herringbone structure on PTCDA, and (d) the planar layered structure on PTCDA.

the α-herringbone unit cells are displayed with dashed lines and those for planar layered unit cells with solid lines.

In the case of the bulk unit cells, the intermolecular interaction energy within the layer $E_{\leftrightarrow}$ for the α-herringbone structure is lower than that of the interaction energy with molecules in different layers $E_{\updownarrow}$ for the planar layered structure. The level of $E_{\updownarrow}$ for the α-herringbone structure is also much lower than that of $E_{\leftrightarrow}$ for the planar layered structure. Consequently, the α-herringbone structure is more stable than the planar layered structure by ~6%, consistent with the existence of the α-herringbone H_2Pc structure rather than a planar layered structure when H_2Pc molecules are deposited on noninteracting substrates.[8] For the H_2Pc unit cells on PTCDA, however, the total-energy levels are reversed since the $E_{\updownarrow}$ level for the α-herringbone unit cell on the PTCDA layer is higher than that in the corresponding bulk structure, while the $E_{\updownarrow}$ level for the planar layered unit cell on PTCDA is lower than in the bulk planar structure. During the initial stage of H_2Pc deposition on a planar PTCDA layer, this minimum-energy difference seems to determine the structure of the H_2Pc films. For the monolayer deposition of H_2Pc on PTCDA, the total energy of the planar layered film is -290.8 kJ/mol, which is ~9% more stable than that of the α-herringbone structure -267.2 kJ/mol. This result provides an excellent quantitative explanation for our recent experimental observations[19,20] for the existence of a planar H_2Pc molecular layer when grown on an initial, planar PTCDA thin film.

The calculations for the energy levels of these four different H_2Pc unit-cell models suggest that once the planar PTCDA layer is formed, subsequent H_2Pc molecules stack parallel to the underlying PTCDA layer in order to enhance the intermolecular interactions between the two layers and hence lower the potential energy of the system.

IV. CONCLUSIONS

H_2Pc molecules form herringbone structures when deposited on noninteracting substrates such as glass, whereas they stack layer by layer when deposited on a planar PTCDA layer. This structural modification caused by the underlying molecular layer gives rise to a structural templating effect. We have calculated the intermolecular interaction energies of four different H_2Pc unit-cell models in order to quantify the templating effect for the H_2Pc/PTCDA heterolayer structure.

For bulk unit cells, the α-herringbone H_2Pc structure is more stable (by ~6%) than the planar layered H_2Pc structure, consistent with the existence of the α-herringbone structure when H_2Pc is grown on noninteracting substrates. By contrast, the planar H_2Pc structure is more stable on PTCDA than the α-herringbone structure (by ~9%), consistent with recent experimental observations of a modified H_2Pc structure. At the energy minimum of the planar layered H_2Pc unit cells, the interplanar stacking distance is calculated to be 3.29 Å, a value very close to the experimentally determined value of 3.33 Å.

Our calculations indicate that the structural templating effect observed in the H_2Pc/PTCDA heterostructure is due to the strong intermolecular interactions between the two different molecular materials at the heterointerface.

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*FAX: +44-20-7594-5801. Email address: t.jones@ic.ac.uk

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