Optical absorption signature of a self-assembled dye monolayer on graphene

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Abstract
A well-organized monolayer of alkylated perylene-3,4,9,10-tetracarboxylic-3,4,9,10-diimide (PTCDI) has been formed onto CVD graphene transferred on a transparent substrate. Its structure has been probed by scanning tunnelling microscopy and its optical properties by polarized transmission spectroscopy at varying incidence. The results show that the transition dipoles of adsorbed PTCDI are all oriented parallel to the substrate. The maximum absorption is consistent with the measured surface density of molecules and their absorption cross section. The spectrum presents mainly a large red-shift of the absorption line compared with the free molecules dispersed in solution, whereas the relative strengths of the vibronic structures are preserved. These changes are attributed to non-resonant interactions with the graphene layer and the neighbouring molecules.

Introduction
Close-packed assemblies of dye molecules exhibit drastically altered photonic properties as compared with the isolated or diluted species [1]. These changes find their origin in near-field optical interactions between the constituent molecules, as early predicted by McRay and Kasha [2]. A well-known example is the spectral shift induced by the self-association of cyanine dyes in solution [3]. Depending on the aggregation pattern of the dyes, either bathochromically shifted $J$-bands or hypsochromically shifted $H$-bands are formed, corresponding to collectively excited states and energy bands of delocalized excitons [4,5]. The giant transition dipole moments associated with such excitations result in enhanced optical interactions, e.g., with plasmon resonators in which case a strong-coupling regime can then be reached [6,7]. These collective excitations can also lead to remarkable light emission processes such as superradiance [8]. Interactions between a dye and its surroundings at the molecular scale may also induce drastic changes in its photonic properties. Structural planarization of the adsorbed molecules
Figure 1: Structural characterization of the substrates. STM images (2.3 × 2.3 nm²) of a HOPG surface (a) and CVD monolayer graphene transferred onto a fused quartz plate (b: 2.3 × 2.3 nm² and c: 50 × 50 nm²). The images were acquired under air atmosphere, in the height (constant current) mode. The setpoint current was $I_{S} = 100$ pA, and the bias was $V_{T} = 200$ mV. The height scale is also shown for graphene on quartz (c).
The PTCDI molecule has become a paradigm both as a self-assembly tecton and as a dye. For the present study, we chose an alkylated form of this dye, \(N,N'\)-ditridecylperylen-3,4,9,10-tetracarboxylic diimide (PTCDI-C13), in order to take advantage of the interactions between \(n\)-alkyl chains and graphitic substrates for forming a spontaneously self-assembled monolayer at the interface between the solution and graphene. The monolayer structures have been studied by STM at the solution–substrate interface. Intramolecular resolution is possible both with HOPG and graphene as substrates (Figure 2). As expected from the atomically flat surface of HOPG, this substrate produces the largest domains. It permits an accurate determination of the lattice parameters, which correspond to a surface density of 0.45 molecules per \(\text{nm}^2\) and a distance between closest neighbours of ca. 1.4 nm. The network obtained on CVD graphene is compatible with that obtained on HOPG, with one molecule per unit cell. The various domains have a finite number of lattice orientations, indicating an epitaxial relationship with the graphitic lattice. These results are fully consistent with the expected formation of a self-assembled monolayer in which the molecules are lying flat on the substrate, with adsorbed \(n\)-alkyl chains aligned on the C-atom lattice. By randomly inspecting various regions of drop-cast samples, it appears that a nearly complete coverage (about 80–90\%) is obtained whereas the droplet spread on the sample contained the exact quantity of molecules needed to form a monolayer (see Experimental section). The quantitative formation of multilayers can thus be ruled out.

Transmission spectra

The solution spectrum of PTCDI-C13 is reported in Figure 3 (labelled “SOL”). It presents the typical vibronic structure.
of a \(\pi-\pi^*\) transition, with an energy difference of 0.18 eV (ca. 1450 cm\(^{-1}\)) between 0–0, 0–1 and 0–2 sub-bands which is a characteristic of the \(\pi\)-conjugated systems as present in the PTCDI core [33]. The main peak is the 0–0 at 2.35 eV and corresponds to an absorption cross section \(\sigma_{\text{SOL}} = 3.3 \times 10^{-16} \text{ cm}^2\) consistent with the molar attenuation coefficient reported in the literature for alkylated PTCDI [34]. Quantum chemical calculations have shown that the transition dipole moment corresponding to the \(\pi-\pi^*\) transition is aligned along the N–N’-axis [33].

The difference transmission spectra between self-assembled monolayer on a substrate of monolayer CVD graphene transferred onto fused quartz are shown in Figure 3. Two types of depositions are reported: (i) drop casting of a droplet of a toluene solution containing the exact amount of molecules needed for a coverage of 0.45 molecule per nm\(^2\) (SAM 1) and (ii) dip-coating in a ca. \(10^{-5}\) M solution in toluene followed by rinsing in toluene and ethanol (SAM 2). The transmission spectra of SAM1 and SAM2 are nearly identical and correspond to a rigid bathochromic shift of 0.14 eV (1130 cm\(^{-1}\)) of the whole vibronic system. This quantitative similarity further supports the homogeneous formation of one monolayer by dip coating, as was shown in the case of drop casting. At the maximum of the 0–0 absorption peak, shifted to 2.21 eV, the relative transmission \(\Delta T/T\) is ca. 2.1% (SAM 1) and ca. 1.9% (SAM 2). For an absorbing monolayer deposited on a lossless dielectric substrate, the relative transmission depends only on the absorptive part of the molecular optical response [35]. Given the molecule surface density of 0.45 molecule per nm\(^2\) measured by STM, the molecular absorption cross section can be thus evaluated to \(\sigma_{\text{ML}} = 4.5 \times 10^{-16} \text{ cm}^2\). By assuming an in-plane orientation of the N–N’-axis, which gives a factor of 3/2 corresponding to a 2D orientational averaging of the transition dipole moments instead of the 3D averaging in solution, the above value is fully consistent with that obtained in solution (3.3 \(\times\) \(10^{-16}\) cm\(^2\)). Notice that accounting for the Lorentz local field correction to \(\sigma_{\text{SOL}} = [(n^2 + 1)/3]^{\pi/\pi^*} n\) with \(n\) being the index of refraction of toluene, and for the substrate-index correction to \(\sigma_{\text{ML}} = (n + 1)/2\) with \(n\) being the index of the substrate [35], does not change this conclusion (ca. 1.33 and ca. 1.25, respectively). Microspectroscopy sampling of the sample, averaged over a spot of about 3\(\mu\)m in diameter have shown a high homogeneity of the absorption in the range of millimetres.

Remarkably, in the absence of graphene coverage on the fused-quartz substrate prior to PTCDI-C13 deposition, completely different transmission spectra are observed. Actually, no measurable absorption is recorded after using the dip coating technique and the spectrum observed for drop casting is very similar to the one reported in the literature for PTCDI microcrystalline films [36] (µC, solid and dotted lines). Moreover, microspectroscopy has shown a high inhomogeneity of the absorption strength, whereas the measured spectra acquired at different places remain homothetic.

Finally, we have measured the dependence of the incidence angle of the PTCDI absorption spectral feature in the polarized absorption for SAM1 and SAM2 samples (Figure 4). Whereas the absorption increases with incidence for TE polarization (blue triangles in Figure 4), it decreases monotonically with increasing incidence for TM polarization (red squares). In both cases, the molecule spectrum changes homothetically, that is preserving the balance between vibronic peaks. These observations confirm that the orientations of the transition dipole moments of the molecule are parallel to the substrate surface (graphene layer), as shown by the theoretical model [37] (continuous lines). This effect is even visible to the naked eye looking through a tilted plate through a polarizer. Notice that, for a thin film with random 3D molecule orientation, both TE and TM polarizations should exhibit an increased absorption at grazing incidence.

![Figure 4: Optical signature of orientations of self-organized PTCDI-C13. Variable-incidence polarized-transmission analysis of the contribution of the self-assembled molecular monolayer to the absorption (blue triangle: TE, red squares: TM). The optical density at the absorption maximum (\(\lambda = 561\) nm), as obtained from a fit of the absorption line of the molecule, is plotted. The continuous lines represent the TE and TM theoretical absorption variations [37] considering molecular transition dipole moments lying flat on graphene. For randomly-oriented transition dipole moments, both TE and TM should increase with incidence following the blue line.](image)
assembled onto the graphene substrate with a planar geometry of the molecules. The most striking feature of the self-assembled monolayer spectra is the uniform red-shift of the whole vibronic spectral line, which results from the self-assembly. This shift is not accompanied by an important blurring of the spectral structures, consistent with the high homogeneity of molecular organization and environments obtained through the atomically precise self-assembly process on graphene. The energy difference between 0–0, 0–1 and 0–2 sub-bands is preserved, at 0.18 eV. This value is characteristic of the π-conjugated C–C double bond vibration and shows that the absorption remains dominated by the π–π* transition.

2D ordered aggregation of similar molecules on metals have been reported to induced drastic changes in optical spectra, attributed to new electronic transitions [16]. Less pronounced rigid spectral shifts have been reported previously for molecules deposited on crystalline dielectrics such as hexagonal boron nitride (h-BN) [9,19]. The cited possible origins of such shifts are optical interactions between molecules or between molecules and the substrate and the deformation of molecules induced by van der Waals interactions between molecules and substrate. Intermolecular optical interactions are a consequence of the local electric field resulting from the induced dipoles of molecules at neighbouring sites [38]. For an assembly of molecules in free space, this relative change is

$$\frac{\Delta E}{E} = \frac{C \sigma \lambda}{4\pi d^3},$$

where $\sigma$ is the absorption cross-section (3.3 × 10^{-16} cm^2), $\lambda$ the excitation wavelength in vacuum (ca. 0.5 μm), $d$ the distance between molecules (1.4 nm), and $C$ a geometrical factor typically of the order of unity. This factor is about 50%, which would be more than sufficient to explain the large shift observed here. However, such resonant interactions should also lead to a concentration of the oscillator strength on the 0–0 vibronic transition [39]. Yet, in the present case, a fit of the absorption line accounting for the spectral broadening of the vibronic structures gives an increase of the 0–0 to 0–1 ratio of only about 20%, which is not consistent with the expected exciton delocalization. A substrate-induced planarization was invoked for hydrogen-bonded porphyrins on h-BN [9]. However, the PTCDI molecule already presents a rigid intrinsically planar covalent structure and substrate-induced planarization cannot explain the even larger shift observed here. The graphene has a much larger polarizability than h-BN. Hence, the strongly increased polarizability of the environment [40] compared with the isolated molecules in toluene solution could explain a larger red-shift. Electronic interactions between conjugated π-electron systems of molecule and graphene (π-stacking), as evidenced by STM spectroscopy for non-alkylated PTCDA [28], may also play a role in changes of the optical bandgap. However, alkyl chains present here should reduce such interactions by maintaining the conjugated moiety at a larger distance from graphene. This is substantiated by the preservation of the absorption line-shape and the balance between vibronic contributions. This also means that the strong resonant molecule–molecule interaction evaluated above in free space is thus screened by the presence of the highly polarizable graphene substrate. These interpretations are consistent with the observation of a concentration of the oscillator strength for dense assemblies of PTCDA deposited on a dielectric substrate [18], in which case no significant spectral shift was observed. An exciting perspective could be given by hexagonal boron nitride (h-BN) monolayers, which combine a dielectric nature with an atomic-scale template similar to that of graphene [41].

**Conclusion**

In conclusion, we have realised the self-assembly of alkylated PTCDA molecules onto a monolayer CVD graphene transferred on a transparent substrate. The molecules form a well-organized dense assembly, the parameters of which being accurately determined by STM. The polarized optical transmission spectra have been acquired at variable incidence thanks to the high optical transparency of the monolayer CVD graphene substrate. This confirms that the transition dipoles of adsorbed PTCDA are all oriented parallel to the substrate. The absorption is consistent with the measured density of molecules and presents mainly a rigid red-shift of the absorption line compared with the free molecules dispersed in solution. These changes are attributed to non-resonant interactions with the graphene layer and the neighbouring molecules.

**Experimental**

The HOPG sample grade ZYB was purchased from SPI and the monolayer CVD graphene transferred onto transparent PET and fused silica samples were purchased from Megan-Technologies (Poland) and Graphenea (Spain), respectively. Both have been transferred from their copper CVD substrate using the standard PMMA technique [42]. The CVD graphene is polycrystalline, with typically 1 μm sized 2D domains. The PET/silica coverage by CVD graphene is ca. 95%.

$N,N'$-Ditridecylperylene-3,4,9,10-tetracarboxylic diimide (PTCDI-(C13)) was purchased from Sigma-Aldrich and used as received. It was dissolved in phenylcyclohexane (99%, Chemos GmbH) for liquid–solid STM experiments or toluene (99.9%, Sigma-Aldrich) for monolayer depositions by drop casting or dip coating. For drop-casting experiments, the concentrations were adjusted so that the applied 5 µL droplet contains the quantity of molecules contained in a monolayer covering the
entire 1 cm² substrate, given the monolayer surface-density measured by STM (0.45 molecule per nm²). This target concentration evaluates to about 1.5 × 10⁻⁵ mol·L⁻¹ and was adjusted with absorption spectroscopy applying the Beer–Lambert law with a molar absorptivity of ε = 87000 L·mol⁻¹·cm⁻¹ for various alkylated PTCDI [34]. For dip-coating experiments, the samples were immersed for 1 min in a toluene solution with the same concentration as for drop casting, and then gently rinsed with neat toluene for typically 5 min. The transferred monolayer CVD graphene remained unaltered even after prolonged immersion in toluene. Hence only the upper side of the graphene is exposed to the PTCDI solution.

The STM images were recorded under ambient conditions (ca. 300 K) with a custom-made digital system by the immersion of a 250 μm mechanically cut tip of Pt/Ir (90/10) purchased from Goodfellow into a 5 μl droplet of solution. The scanning piezo-electric ceramic was calibrated by means of atomic resolution obtained on HOPG images in XY-directions and with flame-annealed gold through the height of steps in the Z-direction. All the images were obtained at a quasi-constant current, i.e., in the variable-height mode. The images in Figure 1a,b were corrected for the thermal drift by combining two successive images with downward and upward slow-scan directions.

Optical absorption spectra at normal incidence were obtained with a Perkin-Elmer Lambda 650 spectrometer. Optical microspectroscopy was adapted on an Olympus IX71 microscope equipped with an Ocean Optics spectrometer QE-Pro. Variable incidence measurements were acquired on a custom-made goniometer bench using the same spectrometer, by monitoring the absorption at its maximum, at λ = 560 nm.

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