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DEMONSTRATION OF HETEROEPITAXY OF BIPHENYL OVERLAYER BY VARYING THE DEPOSITION TEMPERATURE OF XYLENE SUBSTRATE ON Al_2O_3

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Abstract

Vapor deposition of pure biphenyl on a single crystal of Al_2O_3 between 110–115 K prepared the biphenyl in the twisted conformation with $\lambda_{max} \approx 320$ nm. Deposition at 130 K allowed biphenyl to overcome the activation barrier to planarity but was sufficiently amorphous to form excimer with a characteristic $\lambda_{max} \approx 370$ nm. When biphenyl was deposited at 160 K, the thermal energy was sufficient to undergo the disorder-to-order transition such that the adlayer was composed of biphenyl in the planar conformation with $\lambda_{max} \approx 345$ nm which was analogous to the solid crystal. The transition was accompanied by a decrease in the fluorescence intensity due to energy transfer within the ordered matrix. A thin layer of *m*-, *o*- or *p*-xylene was deposited at temperatures that varied between 105–150 K upon which biphenyl was deposited as a thick layer. The degree to which ordering occurred in the substrate was sensitive to the deposition temperature and in turn determined the conformer and ordering of the biphenyl overlayer. In addition the passage of the xylene through the crystalline biphenyl epilayer increased the density of defect sites and resulted in enhanced fluorescence intensity.

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Introduction

Epitaxy is a method by which the growth of crystals is controlled by vapor deposition of overlayer on a substrate the possesses the desired crystallographic characteristics (1-4), but research on and application of epitaxy of smaller aromatic molecules such as biphenyl have been sparse because of the lack of phase stability due to their high vapor pressure. Yet, biphenyl is an interesting molecule because its conformation, i.e. planar or twisted, can be readily determined by its fluorescence spectra (5-7). Recently the crystal growth of biphenyl on Al_2O_3 was controlled by manipulating the ordering in the substrate by varying the deposition temperature (5-7). In part one of this study, homoepitaxy was demonstrated with the deposition of biphenyl overlayer on biphenyl substrate in which the crystal form of biphenyl substrate was controlled by the deposition temperature (8). In this paper, the heteroepitaxial crystallization of biphenyl on each of the three isomers of xylene is demonstrated by utilizing the spectral signatures of the excimer, twisted and planar conformations of biphenyl on Al_2O_3.

Experimental

Biphenyl, *o*-xylene, *m*-xylene, *p*-xylene were of the highest purity that were commercially available, typically > 99% (Sigma-Aldrich, St. Louis, MO). These compounds were placed in separate sample holders and vapor deposition was accomplished with adjustable precision leak valves. Details of the experimental set up have been previously published (5-7) and a brief summary is given here. The ultra-high vacuum chamber had a background hydrogen base pressure of 1×10^{-9} Torr. A single crystal of Al_2O_3 (0001) (Crystal Systems, Inc., Salem, MA) was suspended on the lower end of a liquid nitrogen cryostat via copper post on either side of the Al_2O_3 with a sapphire spacer for electrical and thermal isolation. The sapphire spacer partially isolated the liquid nitrogen thermally from the crystal so that the lowest temperature that was routinely achieved was about 110-115 K. Temperatures as low as 105 were accessible by pumping on the liquid nitrogen reservoir. For the experiments in which a substrate was deposited at varying temperatures, the temperature was controlled to within ± 1 K by feedback algorithm described below. The sample was cooled to 110-115 K prior to the epilayer deposition and then the temperature programmed desorption (TPD) was performed. During the TPD experiment, the temperature was linearly ramped at 2 K/s by resistively heating the Al_2O_3. This was accomplished by sending current through a thin tantalum foil that was in thermal contact with it. A type-K (chromel/alumel) thermocouple (Omega, Norwalk, CT) that was also in thermal contact with the Al_2O_3 monitored the temperature. Process control during the TPD experiment was accomplished by a program written in LabVIEW (National Instruments, Austin, TX) that incorporated a PID (proportional-integral-derivative) feedback algorithm that linearly incremented the temperature of the Al_2O_3 crystal.

Additionally during the TPD, the program took the fluorescence spectra from an Ocean Optics USB4000 spectrometer (Ocean Optics, Dunedin, FL) in real time every 300 ms. The program also scanned the residual gas analyzer for the masses of the compounds that had been deposited onto the Al_2O_3. Manipulation of the array of spectra as a function of temperature by a MATLAB (Mathworks, Natick, MA) template yielded the wavelength-resolved TPDs that are shown in the figures. To ensure a clean surface, the Al_2O_3 was heated to 300 K after each run. Temperature ramps to higher temperatures did not indicate any other adsorbates. The linearity in the ramp was continuously monitored during each run.

The activation energy for desorption, E_a, was calculated by Redhead analysis (9) in which a first-order desorption kinetics as described by King (11) was assumed and is based on the mass spectral peak desorption temperature, T_p (10). The uncertainties in the desorption temperatures lead to a propagated error in the activation energies of ± 2%.

The surface coverages, Θ, in monolayers (ML) were calculated by calibrating the integrated mass spectral peaks to an optical interference experiment. The interference experiment yielded accurate rate of deposition with coverage error of ± 30%, and is described in detail elsewhere (12).

To demonstrate heteroepitaxy, a layer of xylene substrate was deposited at varying temperatures, 105 to 150 K, at a coverage as close to 25 ML as possible. The substrate was cooled to 110-115 K and the biphenyl overlayer was deposited at a coverage as close to 100 ML as possible. Then the TPD experiment was performed. Since the planar conformer of the ordered biphenyl has a characteristic fluorescence with $\lambda_{max} \approx 345$ nm, when the spectra exhibited this wavelength epitaxy was achieved. Otherwise, the biphenyl would form the twisted conformer with a characteristic fluorescence with $\lambda_{max} \approx 320$ nm . A higher deposition temperature would predictably form the planar amorphous form, the excimer, with $\lambda_{max} \approx 370$ nm. In these experiments, the temperature of the Al_2O_3 was set to the desired deposition temperature upon which the xylene was vapor deposited. Then the surface was allowed to cool to 110-115 K, at which temperature the biphenyl was deposited on top of the xylene. The TPD experiment was then carried out. Since the xylenes began to desorb at temperatures above 150 K, this was the upper limit to the substrate deposition temperature. The analysis of the intensities of the biphenyl overlayer as a function of deposition temperature of the substrate was done at 120 K during the TPD experiment.

Annealing experiments were done to resolve the relative contributions to the enhanced fluorescence intensity from energy transfer or increase in the density of defect sites due to the passage of xylene through the biphenyl adlayer. The bilayer in which both the substrate and overlayer had been deposited at 100-115 K was annealed for 30 s at a temperature past the desorption temperature of the xylene, cooled to the deposition temperature of 110-115 K and then the TPD performed. The pre-anneal initial intensity was the flurescence intensity of the dominant conformer (either twisted or planar) of biphenyl upon deposition on the substrate at 110-115 K. In other words, when the substrate was biphenyl, the dominant fluorescent species was the twisted conformer observed at $\lambda_{max} \approx 320$ nm and when the substrate was *p*-xylene, fluorescence was that of the excimer at $\lambda_{max} \approx 370$ nm. In order to have a benchmark for a molecule that will not undergo energy transfer, but will potentially cause an increase in the density of defect sites due to its passage through the biphenyl adlayer, two aliphatic molecules were chosen as analogues of *p*- and *o*-xylenes, *trans*-1,4-dimethylcyclohexane and *cis*-1,3-dimethylcyclohexane, (DMCH) respectively.

Results and Discussion

Epilayer: multilayer biphenyl

The wavelength-resolved TPD of biphenyl with $\Theta_{biphenyl} \approx 49$ ML that was deposited at 130 K, and the overlayer of biphenyl at 100 ML that was deposited at 115 K is shown in Figure 1 as a representative of biphenyl is in it's various conformer. Here, it begins as a excimer with $\lambda_{max} \approx 370$ nm, undergoes a disorder-to-order transition and ends in a planar conformer with $\lambda_{max} \approx 345$ nm. A summary of the main features that were observed in these wavelength-resolved TPD plots where the deposition temperature was varied were:

1). Although not shown here, with a $\lambda_{max} \approx 320$ nm, the fluorescence of the amorphous adlayer at a deposition temperature of 110-115 K was previously characterized to be the twisted conformer (12,13).

2). The disorder-to-order transition occurred at 160 ± 1 K with $\Theta_{biphenyl} = 98 \pm 16$ ML at which temperature biphenyl assumed a planar conformation and had a $\lambda_{max} \approx 345$ nm (12,13). If the fluorescence quantum yields were assumed to be the same for the planar and non-planar conformers, energy transfer within the ordered adlayer resulted in intensity loss to about 15% relative to that at deposition (12,13).

3). In a separate experiment, adlayer of biphenyl that was deposited at 130 K was amorphous and in the planar conformation, both of which are necessary requirements for the formation of excimers (13) and the fluorescence λ_{max} red-shifted to ≈ 370 nm. The optimum deposition temperature for the formation of the excimer was about 138 K (13). As shown in Figure 1, the overlayer has been formed in the conformer of the substrate, since it was deposited at a temperature that favored the excimer.

The fluorescence intensities from the three forms of biphenyl, amorphous twisted (x), amorphous planar (excimer) (▲) and ordered planar (●) are shown in Figure 2 as a function of deposition temperature of the biphenyl substrate at 44 ± 15 ML and the overlayer of biphenyl that had been deposited at 103 ± 13 ML at 115 ± 1 K. For neat biphenyl the twisted conformer-to-planar excimer crossover temperature occurred at about 124 K and the ex-

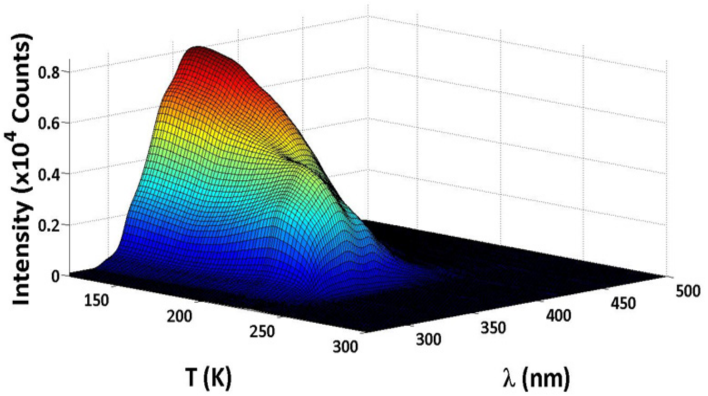

Figure 1. Wavelength resolved TPD of biphenyl bilayer in which biphenyl at $\Theta_{biphenyl} \approx 49$ ML that was deposited at 130 K and the overlayer of biphenyl at 100 ML that was deposited at 115 K.

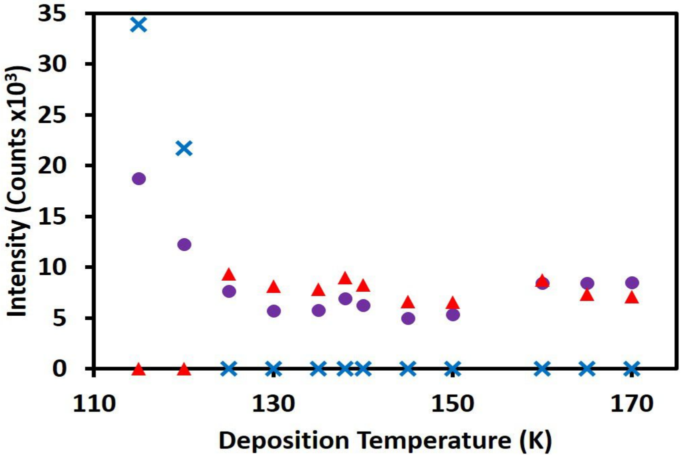

Figure 2. The initial intensities (photon counts) from the three forms of biphenyl, amorphous twisted (x), amorphous planar (excimer) (▲) and ordered planar (●) as a function of deposition temperature for biphenyl substrate coverages of $\Theta_{biphenyl} \approx 44 \pm 15$ ML and the overlayer of biphenyl was deposited at $\Theta_{biphenyl} \approx 103 \pm 13$ ML at 115 ±1 K.

cimer-to-planar ordered crossover temperature occurred at about 165 K. In order to compare the effect of other substrates with that of Al_2O_3 on the epitaxial growth of the biphenyl overlayer, the crossover temperatures will be used as a qualitative measure of the substrate morphology.

Substrate: multilayer xylenes

The fluorescence spectra of neat xylenes were published elsewhere (13,14) and only briefly described here. The most intense fluorescence peaks for *m*-xylene, *o*-xylene and *p*-xylene were centered at 284 nm, 282 nm and 286 nm, respectively (13,14). For all three multilayers, the fluorescence increased as functions of coverage (13,14). All three xylenes showed phosphorescence in the > 400 nm region (13,14). Low coverage peak desorption temperatures for *m*-xylene, *o*-xylene and *p*-xylene were 180.7 K, 187.3 K, 192.8 K, for which the activation energies of desorption were 43.0 kJ, 44.0 kJ and 44.6 kJ respectively (9-11,13,14).

Bilayer: m-xylene substrate/biphenyl epilayer

Shown in Figure 3 is a wavelength-resolved TPD of *m*-xylene/biphenyl bilayer with $\Theta_{m\text{-xylene}} \approx 29$ ML that had been deposited at 130 K and biphenyl epilayer with $\Theta_{\text{biphenyl}} \approx 92$ ML that had been deposited at 115 K. The twisted conformer of biphenyl with $\lambda_{max} \approx 320$ nm dominated the spectrum. Shown in Figure 4 is the fluorescence intensities from the three forms of biphenyl, amorphous twisted (**x**), amorphous planar (excimer) (▲) and ordered planar (●) as functions of *m*-xylene deposition temperature with $\Theta_{m\text{-xylene}} \approx 34 \pm 8$ ML and the epilayer of biphenyl with $\Theta_{\text{biphenyl}} \approx 100 \pm 8$ ML that had been deposited at 115 ± 1 K. Here the twisted conformer of biphenyl overlayer persisted through the deposition temperatures of the substrate. Since the twisted conformer of biphenyl was observed in the neat biphenyl that had been deposited at 115 K, the tentative conclusion was that the *m*-xylene substrate was in disorder that persisted through the deposition temperatures and that a disorder-to-order transition did not occur.

Bilayer: o-xylene substrate/biphenyl epilayer

Shown in Figure 5 is the wavelength-resolved TPD of bilayer of *o*-xylene/biphenyl at 130 K with $\Theta_{o\text{-xylene}} \approx 38$ ML and the epilayer with $\Theta_{\text{biphenyl}} \approx 88$ ML that had been deposited at 115 K. Shown in Figure 6 is the fluorescence intensities from the three forms of biphenyl, amorphous twisted (**x**), amorphous planar (excimer) (▲) and ordered planar (●) for the *o*-xylene substrate that had been deposited as different temperatures with $\Theta_{o\text{-xylene}} \approx 39 \pm 7$ ML with

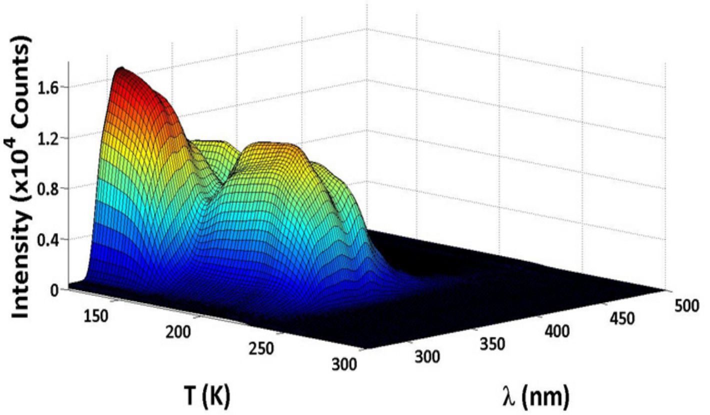

Figure 3. Wavelength resolved TPD of *m*-xylene for ≈ 29 ML of *m*-xylene substrate that had been deposited at 130 K upon which ≈ 92 ML of biphenyl was deposited at 115 K.

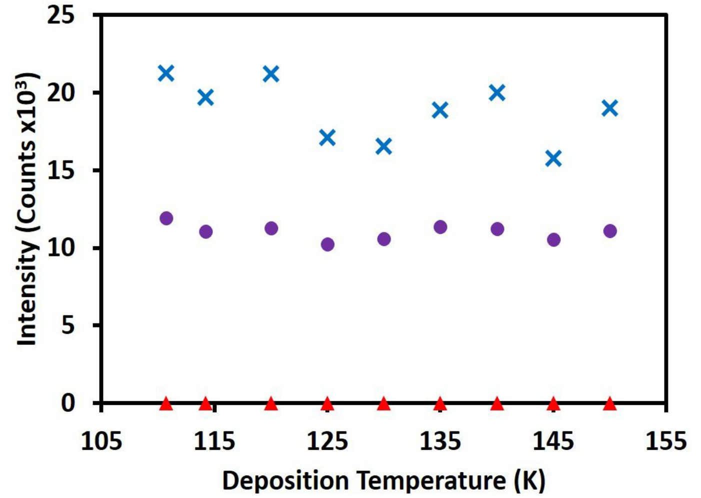

Figure 4. The initial intensities (photon counts) for the three forms of biphenyl, amorphous twisted (**x**), amorphous planar (excimer) (▲) and ordered planar (●) as a function of deposition temperature for substrate coverages of *m*-xylene with $\Theta_{m\text{-xylene}} \approx 34 \pm 8$ ML with $\Theta_{\text{biphenyl}} \approx 100 \pm 8$ ML that had been deposited at 115 ±1 K.

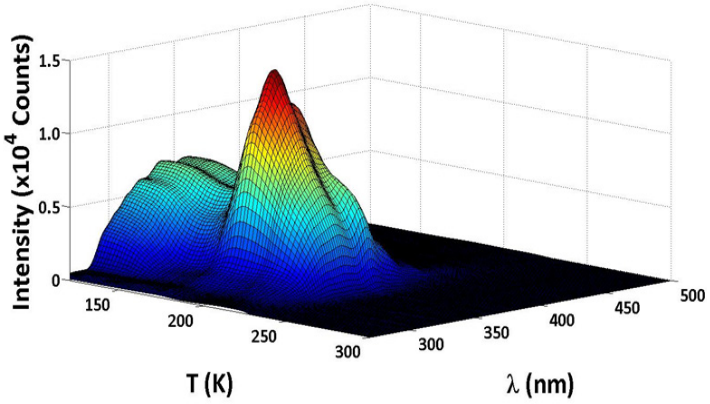

Figure 5. Wavelength resolved TPD of *o*-xylene/biphenyl bilayer with $\Theta_{o\text{-xylene}} \approx 38$ ML and the epilayer at 130 K with $\Theta_{\text{biphenyl}} \approx 88$ ML that had been deposited at 115 K

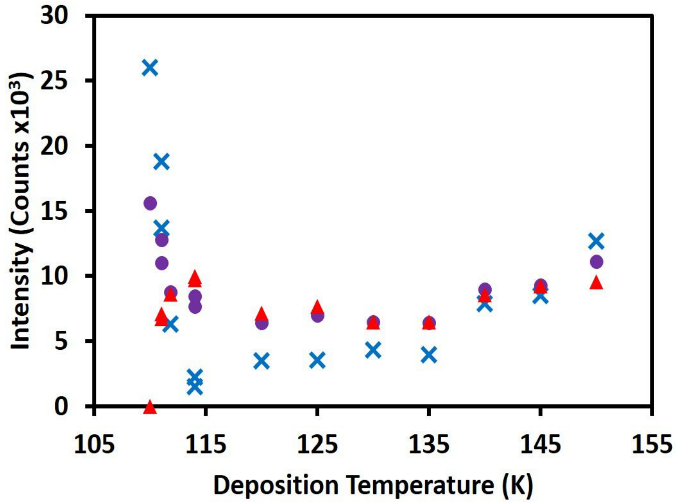

Figure 6. The initial intensities (photon counts) from the three forms of biphenyl, amorphous twisted (**x**), amorphous planar (excimer) (▲) and ordered planar (●) as a function of deposition temperature for coverages of *o*-xylene substrate at $\Theta_{o\text{-xylene}} \approx 39 \pm 7$ ML with $\Theta_{\text{biphenyl}} \approx 102 \pm 8$ ML that had been deposited at 114 ± 2 K.

$\Theta_{\text{biphenyl}} \approx 102 \pm 8$ ML epilayer that had been deposited at 114 ± 2 K. As with *m*-xylene/biphenyl bilayer, at low substrate deposition temperatures, the biphenyl overlayer began the TPD in the twisted conformation with $\lambda_{\text{max}} \approx 320$ nm. The crossover temperatures were 112 K for the twisted conformer to planar amorphous excimer. The second crossover temperature occurred at about 145 K. Comparison of Figures 2 and 6 showed the qualitative similarities of *o*-xylene and biphenyl as substrates. When both the sensitivity of the biphenyl epilayer to the substrate morphology and the observation of crossover temperatures in the biphenyl overlayer are considered, a tentative conclusion can be made that the *o*-xylene substrate in this bilayer underwent an ordering transition at ~ 112 K, the first crossover temperature.

Bilayer: p-xylene substrate/biphenyl epilayer

Figure 7 shows the wavelength-resolved TPD of the bilayer that had the *p*-xylene substrate deposited at 130 K with $\Theta_{p\text{-xylene}} \approx 36$ ML and the epilayer with $\Theta_{\text{biphenyl}} \approx 100$ ML that had been deposited at 115.5 K.

Shown in Figure 8 are the intensities as a function of deposition temperature of planar excimer (▲), twisted (**x**) and ordered planar (●) conformers of biphenyl with $\Theta_{\text{biphenyl}} \approx 97 \pm 9$ M that had been deposited at 114 ± 3 K as a function of the deposition temperatures of the *p*-xylene substrate with $\Theta_{p\text{-xylene}} \approx 41 \pm 8$ ML. The crossover temperature for the twisted conformer to planar excimer was at about 108 K which was the lowest observed for the systems under investigation while the crossover temperature for the excimer-to-planar ordered was over 150 K. For systems where biphenyl is the substrate and *p*-xylene is the substrate have comparable temperature widths at the cross over temperatures and the crossover points themselves are lowered by about 15 K for *p*-xylene. A tentative explanation for the *p*-xylene's lower crossover temperatures compared to those of biphenyl was that the *p*-xylene exhibited kinetic energy at a lower temperature prior to desorption. In addition, *p*-xylene also underwent an ordering transition.

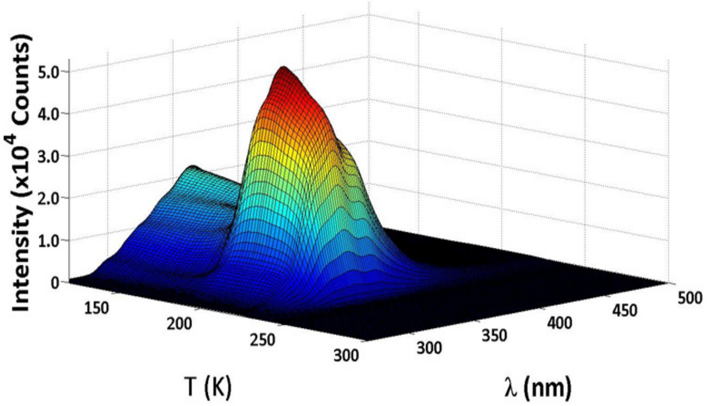

Figure 7. Wavelength resolved TPD of *p*-xylene substrate of $\Theta_{p\text{-xylene}} \approx 36$ ML with the substrate that was deposited at 130 K upon which $\Theta_{\text{biphenyl}} \approx 100$ ML of biphenyl was deposited at 115.5 K.

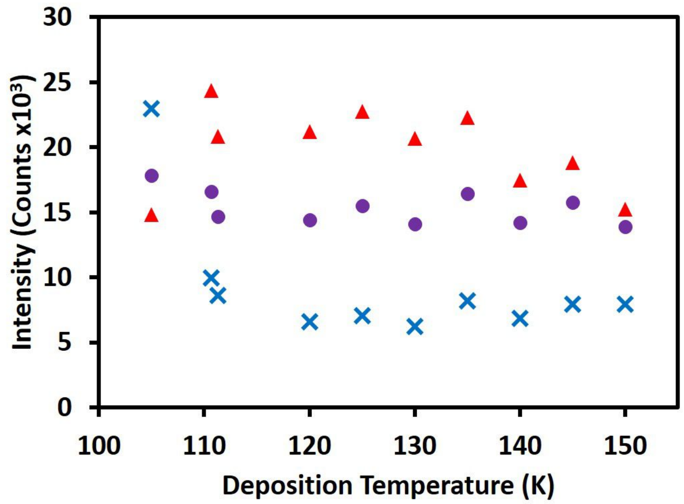

Figure 8. The initial intensities (photon counts) from the three forms of biphenyl, amorphous twisted (**x**), amorphous planar (excimer) (▲) and ordered planar (●) as a function of *p*-xyxlene deposition temperature for coverages of *p*-xylene substrate at $\Theta_{p\text{-xylene}} \approx 41 \pm 8$ ML with $\Theta_{\text{biphenyl}} \approx 97 \pm 9$ ML that had been deposited at 114±3 K.

One notable difference that *p*-xylene/biphenyl bilayer exhibited relative to the other bilayers was the large fluorescence enhancement as the *p*-xylene desorbed through the biphenyl (Cf. Fig. 7, note the difference in the intensity scale). Energy transfer and increase in the density of defect sites were thought to be the two causes for this enhancement (14). The relative contributions from these two causes can be resolved by annealing experiments (Cf. experimental section) and an analysis of the data shown in Figure 9. In each set of histograms, the left most bars are the initial intensities that were measured after deposition of the bilayer with the various substrates and biphenyl overlayer at 110-115 K. The second bar is the maximum intensity of the wavelength resolved TPD that occurred at about 190 K, the temperature at which the adlayers were annealed. Note that all of the xylene will have desorbed at the annealing temperature. Then the adlayer was cooled to 115 K and the intensities given by the bars on the right. For *p*-xylene substrate, the increased intensity of the second bar can be attributed to either energy transfer *or* to increase density of defect sites that was caused by the *p*-xylene's passage through the biphenyl adlayer or to both. The intensity of the fluorescence after the anneal is shown in the third bar, and reflects the intensity due to defect sites that *persisted* after the *p*-xylene had desorbed. Included in the histogram is the anneal experiment from *trans*-1,4-DMCH substrate and biphenyl overlayer. This substrate was chosen as the aliphatic analogue of *p*-xylene for which energy transfer can be assumed to be absent and would only cause an increase in the defect sites in the biphenyl during its passage. The difference in intensities of the

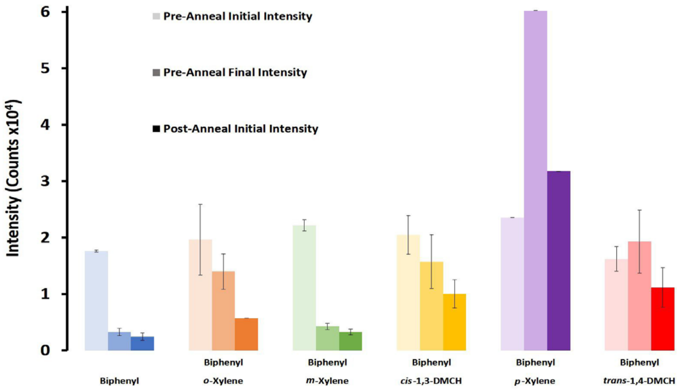

Figure 9. Histogram of various substrates wit bipheyl overlayer. Plots are of pre-anneal initial intensities (left bar), pre-anneal final intensities (the maximum intensities during the anneals, middle bar) and initial intensities after cooling to 115 K after the anneal (right bar), Coverages for substrates and overlayers were 37 ±10 ML and 107 ± 8 ML, respectively.

second and third bars was indicative of the thermal *reversibility* of the defects created by the passage of this substrate. Furthermore, the difference in the right hand bars for *trans*-1,4-DMCH and biphenyl shown in blue is the permanent (irreversible) increase in the defect sites created by the passage of *p*-xylene through the biphenyl layer. Hence, for *p*-xylene/biphenyl bilayer, the proportional increase in the fluorescence intensity can be attributed to the formation of defects, both reversible and permanent. Lastly, less than about 10 % of the increase in intensity of the *p*-xylene/biphenyl bilayer might be due to energy transfer.

When *o*-xylene was the substrate, only a minimal number of defect sites were created whereas for *m*-xylene substrate fluorescence enhancement was absent. For *m*-xylene, the mass spectral data showed desorption at multiple temperatures that were higher than for neat *m*-xylene. One possible explanation for the absence of perturbation of the biphenyl when *m*-xylene is the substrate might be that the *m*-xylene was impeded from desorbing through and instead desorbed around the biphenyl overlayer due to the low *m*-xylene/biphenyl interaction. This might also explain the anomalous result shown in Figure 4 that appeared to exhibit results similar to that when biphenyl itself was the substrate. The aliphatic analogue of *m*-xylene, *cis*-1,4-DMCH as a substrate caused the larger density of defects in biphenyl, presumably because of the out-of-plane hydrogens. Interestingly, mass spectral data during the TPD showed multiple peaks during the passage of *cis*-1,4-DMCH through the biphenyl adlayer, just as *m*-xylene did.

Summary:

As an overlayer biphenyl is a useful sensor of substrate ordering because of the spectral signatures of the two stable conformers: twisted at 320 nm and the planar at 345 nm as well as and excimer at 370 nm. The crossover temperatures from twisted amorphous to planar amorphous for *p*-xylene, *o*-xylene and biphenyl were 108, 112, 126 K, respectively while on *m*-xylene substrate the crossover did not occur. For the xylenes, these observations appear to reflect the strength of intermolecular interaction. This is corroborated by their desorption temperatures and melting points. Peak desorption temperatures were 181, 187 and 193 K for *m*-, *o*- and *p*-xylene, respectively (14), and their melting points are -48, -25 and 13^o C for *m*-, *o*- and *p*-xylene, respectively (16). Open to further investigation is a speculative interpretation that the strong intermolecular interaction for *p*-xylene resulted in the formation of clusters or islands that made a surface that was morphologically rough for the biphenyl overlayer.

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