

DETERMINATION OF TORSIONAL ANGLES OF BIPHENYL MOLECULES ON  $\text{Al}_2\text{O}_3$ 

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## Abstract

Dihedral angles for biphenyl containing molecules were plotted as functions of fluorescence wavelengths of these molecules on  $\text{Al}_2\text{O}_3$ .<sup>1-10</sup> The equation for the best fit line gave an estimate of the dihedral angle from the fluorescence wavelength of any other biphenyl molecule. Since biphenyl becomes more planar on naphthalene than when it had been directly deposited on  $\text{Al}_2\text{O}_3$  due to epitaxy, this equation was used to determine whether sterically hindered 2-methyl and 2,2'-dimethylbiphenyl would compete epitaxially when similarly deposited onto naphthalene. A change of 26° and 29° towards planarity were observed for these molecules on naphthalene, respectively. In addition, they formed van der Waals complexes, or exciplexes, with naphthalene for which the change in dihedral angles of 36° and 56° were observed, respectively. Other biphenyl molecules such as 4-methylbiphenyl exhibited three distinct fluorescence peaks with  $\lambda_{\text{max}}$  of 321, 352 and 372 nm. A variety of methods were used to characterize the nature of these three molecular types during the temperature programmed desorption (TPD). The analyses show that the 4-methylbiphenyl that has the  $\lambda_{\text{max}}$  of 321 nm with a dihedral angle of 37° is associated with the amorphously deposited molecules, while the dominant species in the ordered adlayer has a  $\lambda_{\text{max}}$  of 352 with a dihedral angle of 0°. The species with the  $\lambda_{\text{max}}$  of 372 nm fluorescence is the excimer of 4-methylbiphenyl. The dihedral angle of 31° did not change epitaxially when 4,4'-dimethylbiphenyl was deposited on naphthalene, but did form an exciplex with naphthalene. 3-Methylbiphenyl, with a dihedral angle of 53° became slightly more planar when deposited on planar biphenyl.

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## Introduction

The two phenyl groups in biphenyl can have varying dihedral angles.<sup>1,2</sup> In the gas phase, biphenyl is in the twisted conformer, whereas in the solid crystal, biphenyl has a more planar conformer.<sup>1,2</sup> Previous studies have shown that these conformers gave rise to different fluorescence spectra, so that these spectral signatures can be used to assign biphenyl's conformer when it is vapor deposited on a surface.<sup>1,2</sup> When biphenyl is vapor deposited on  $\text{Al}_2\text{O}_3$  at 110 K, the fluorescence is from the twisted conformer and has a  $\lambda_{\text{max}} = 320$  nm.<sup>3-5</sup> When the surface temperature is ramped in a temperature programmed desorption (TPD) experiment subsequent to deposition, biphenyl undergoes changes in the conformer from twisted<sup>6</sup> to a more planar conformer<sup>7</sup> with  $\lambda_{\text{max}} = 331$  nm during the disorder-to-order transition at 160 K with a concomitant reduction in intensity.<sup>3-5</sup> Finally, if biphenyl is deposited on top of a planar molecule such as naphthalene, it will deposit epitaxially in the planar conformer.<sup>3-5</sup>

The dihedral angles of other molecules that have the biphenyl moiety within the structure, such as 9,10-dihydrophenanthrene<sup>8</sup>, fluorene<sup>9</sup>, 2-methylbiphenyl<sup>10</sup>, 2,2'-dimethylbiphenyl<sup>6</sup>, 4-methylbiphenyl<sup>10</sup> and 4,4'-dimethylbiphenyl<sup>10</sup> have been reported. In Figure 1, these dihedral angles are plotted as a function of the observed fluorescence  $\lambda_{\text{max}}$  of these molecules.<sup>3</sup> From the trend line equation, the torsional angle can be estimated from the observed fluorescence  $\lambda_{\text{max}}$  for any biphenyl containing molecule.

This plot was then applied to an interesting question related to the facility with which biphenyl accommodates an epitaxial underlayer's geometry by overcoming the rotational energy barrier. Just as naphthalene caused biphenyl to become more planar, would it cause the sterically hindered 2-methylbiphenyl and 2,2'-dimethylbiphenyl to also become more planar, or would the rotational energy barrier be too large to overcome when epitaxially depos-

ited on naphthalene. In addition, the  $\lambda_{\text{max}}$ 's of the conformers of 3-methylbiphenyl, 4-methylbiphenyl, 4-ethylbiphenyl and 4,4'-dimethylbiphenyl are interpreted and the surface dynamics on  $\text{Al}_2\text{O}_3$  during the TPD are reported.

## Experimental

Naphthalene, 2-methylbiphenyl, 2,2'-dimethylbiphenyl, 3-methylbiphenyl, 4-methylbiphenyl, 4,4'-dimethylbiphenyl and 4-ethylbiphenyl were of the highest purity that was commercially available. (Sigma-Aldrich, St. Louis, MO; TCI, Pittsburgh, PA; Santa Cruz Biotechnology, Santa Cruz, CA). These compounds were placed in separate sample holders and outgassed by freeze-pump-thaw cycles. Since the  $\text{Al}_2\text{O}_3$  crystal was mounted on a differentially-pumped rotatable high-vacuum adapter, deposition was accomplished by orienting the crystal perpendicularly to tubes attached to high-precision leak valves. These valves were used to quantitatively leak in the vapor from the sample holders into the

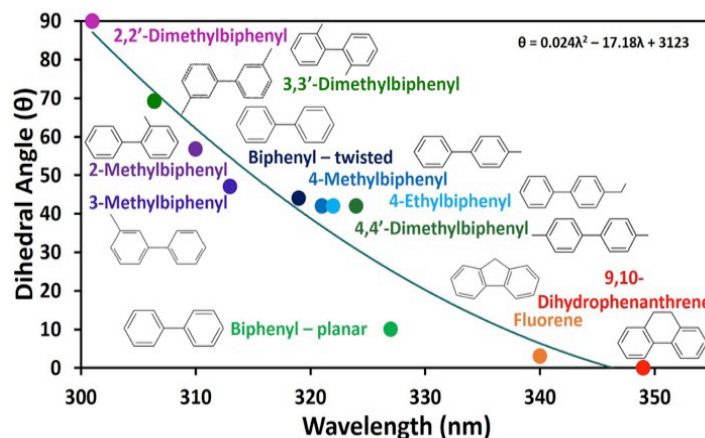


Figure 1. Dihedral angles of biphenyl and related molecules with biphenyl moiety<sup>1,2,6-11</sup> as a function of fluorescence wavelength<sup>3-5</sup>. The trend line equation is shown.

chamber. The chamber was pumped by two turbomolecular pumps configured in tandem backed by a mechanical pump in order to maintain an ultra high vacuum, with background base pressure of nitrogen of  $1 \times 10^{-9}$  Torr.

The temperature programmed desorption experiment was done by ramping the surface temperature by passing current through a tantalum foil that was in thermal contact with the  $\text{Al}_2\text{O}_3$ . A chromel-alumel thermocouple was mounted directly onto the crystal in order to continuously monitor the surface temperature and provided the necessary feedback to generate the linear temperature ramp in the TPD experiment. To ensure a clean surface, the  $\text{Al}_2\text{O}_3$  was heated to 300 K after each run.

Optical pumping was accomplished by filtering the light from a super high-pressure mercury lamp through a 0.25 m monochromator centered on  $250 \pm 10$  nm. The image of the  $\text{Al}_2\text{O}_3$  crystal upon which the fluorophore had been deposited was focused by a quartz lens onto the tip of a fiber optic cable that had been placed inside the vacuum chamber. The fiber cable was fed through a port and the signal was collected by a computer interfaced Ocean Optics spectrometer (Dunedin, FL) that viewed the spectrum every 300 ms. During the TPD, a LabVIEW (National Instruments, Austin, TX) program that had been written in-house took the fluorescence spectra from an Ocean Optics USB4000 spectrometer (Ocean Optics, Dunedin, FL) in real time. The program simultaneously monitored the surface temperature of the  $\text{Al}_2\text{O}_3$  crystal, and through a PID (proportional-integral-derivative) feedback algorithm, linearly ramped the temperature of the  $\text{Al}_2\text{O}_3$  crystal at  $2 \text{ K s}^{-1}$ . The program also scanned the residual gas analyzer for the masses of the compounds that had been deposited on the  $\text{Al}_2\text{O}_3$ . The spreadsheet that comprised the spectra as a function of temperature was transferred to Matlab (MathWorks, Natick, MA) from which the wavelength-resolved TPD figures were made.

The activation energy for desorption,  $E_a$ , was calculated by Redhead analysis in which a first-order desorption kinetics, as described by King, was assumed and was based on the mass spectral peak desorption temperature,  $T_p$ .<sup>11-13</sup> The uncertainties in the desorption temperatures and the propagated error in the activation energies were  $\pm 3\%$ .

The adlayer coverages were determined as follows: the beam from a diode laser was directed at the surface during deposition. As the adlayer thickness increased, an optical interference occurred in the laser beam between the reflected beam at the vacuum - adlayer interface and the adlayer- $\text{Al}_2\text{O}_3$  interface. The integrated mass spectral peaks were calibrated to the optical interference experiment and the coverages,  $\Theta$ , are reported in monolayers (ML) with an error of  $\pm 25\%$ .<sup>3-5</sup> For three molecules, 4-ethylbiphenyl, 3-methylbiphenyl, and 3,3'-dimethylbiphenyl interference experiment failed to yield sufficient intensity and only an approximate conversion factor was used to obtain the coverages; estimates of the error is about  $\pm 50\%$ .

Transmittance experiment was performed by sending part of the excitation light that had passed through the sample to a photomultiplier that was interfaced to an analog-to-digital converter. In this way, the transmitted light intensity was logged during the TPD.

Once deposited, annealed samples were prepared by passing current through the tantalum foil to ramp the temperature to a target value, and then maintaining it for about 5 seconds to anneal the adlayer. The crystal was allowed to cool back down to the deposition temperature, following which the TPD experiment was done.

Vapor deposition at different temperatures from that of the usual 115 K as shown in Figures 14 was performed by ramping to a set temperature and maintained ( $\pm 1$  K) during the deposition. After deposition was completed, the current to the Ta foil was turned off and the sample allowed to cool back to 115 K before the TPD experiment was done.

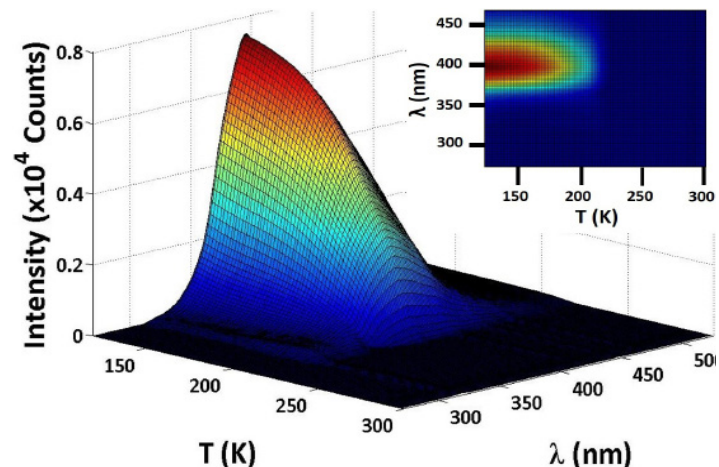
In the plot shown in Figure 1, the error in the torsional angle was determined from the uncertainty in the  $\lambda_{\text{max}}$  which is about 1 nm. This uncertainty resulted in an error of  $\pm 2^\circ$  in the angle and should be noted when the uncertainty is not explicitly stated. If a negative dihedral angle was determined by the trend line equation,  $0^\circ$  was reported.

For the epitaxial experiments, the underlayer was deposited first, followed by the substituted biphenyl. Naphthalene underlayer was deposited at 115 K. For biphenyl, the underlayer was either deposited at 138 K to form the biphenyl excimer which was nearly planar,  $3^\circ$ , or it was annealed at 170 K, which was past the disorder-to-order transition, in which case the dihedral angle was  $25^\circ$ .

## Results and Discussion

### *Naphthalene and 2-methylbiphenyl multilayers and naphthalene/2-methylbiphenyl bilayer:*

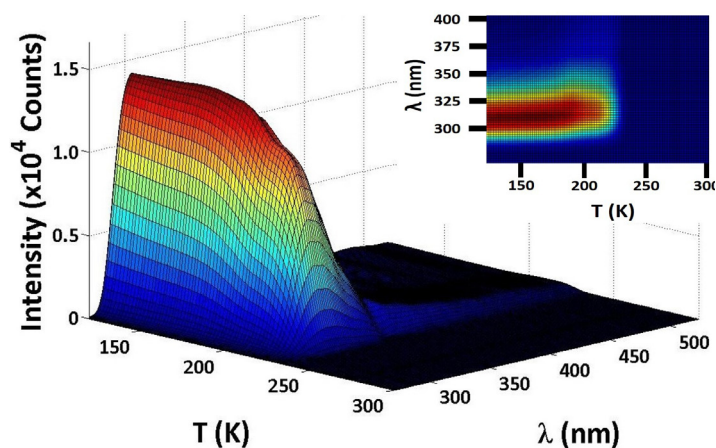
The wavelength-resolved TPD of naphthalene multilayer (neat) that had been vapor deposited with a coverage of  $\Theta_{\text{naphthalene}}$  of 65 ML is shown in Figure 2. Upon deposition, the excimer fluorescence origin was observed at  $\lambda_{\text{max}} \sim 398$  nm. The mass spectrometer was used to determine the peak desorption temperature,  $T_p$ , which was 216 K. First-order desorption was assumed and the activation energy for desorption,  $E_a$ , was calculated to be 54.9 kJ/mol.<sup>11-13</sup>



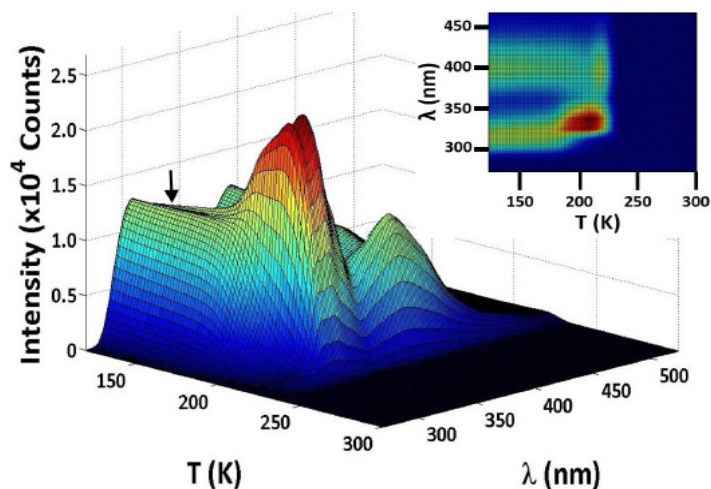
**Figure 2.** Wavelength resolved TPD of multilayer naphthalene.  $\Theta_{\text{naphthalene}} = 65$  ML. The fluorescence at  $\lambda_{\text{max}} \sim 398$  nm is due to the excimer as seen in the inset which is the top view.

The wavelength-resolved TPD of 2-methylbiphenyl multilayer at  $\Theta_{2\text{-methylbiphenyl}}$  of 99 ML is shown in Figure 3. Upon deposition, the fluorescence was observed at  $\lambda_{\text{max}} \sim 310$  nm. As can be seen from the inset to Figure 3, the fluorescence  $\lambda_{\text{max}}$  remained fixed through the TPD. The trend line from Figure 1 gave a dihedral angle of  $63^\circ$  at this wavelength. The peak desorption temperature,  $T_p$ , was 227 K. First-order desorption was assumed and the activation energy for desorption,  $E_a$ , was calculated to be 58.7 kJ/mol.<sup>11-13</sup>

As shown in Figure 4, when 2-methylbiphenyl was deposited on naphthalene, a new fluorescence peak was observed at  $\lambda_{\text{max}} \sim 321$  nm the dihedral angle of which was calculated to be  $37^\circ$ . This angle was  $26^\circ$  more planar than in the multilayer 2-methylbiphenyl. A plot of the fluorescence intensity at 321 nm as a function of the ratio of  $\Theta_{2\text{-methylbiphenyl}}$  to  $\Theta_{\text{naphthalene}}$  is shown in Figure 5. Here,  $\Theta_{\text{naphthalene}}$  was kept constant at  $74 \pm 14$  ML while  $\Theta_{2\text{-methylbiphenyl}}$  was varied. The intensity of 2-methylbiphenyl fluorescence increased with coverage of 2-methylbiphenyl and continued to do so past that which is shown in the figure. The ever increasing intensity



**Figure 3.** Wavelength resolved TPD of  $\Theta_{2\text{-methylbiphenyl}}$  of 99 ML of neat 2-methylbiphenyl. Inset: top view. Note that the  $\lambda_{\text{max}} \sim 310$  nm fluorescence is constant through the entire TPD.



**Figure 4.** Wavelength resolved TPD of bilayer with 2-methylbiphenyl on top of naphthalene.  $\Theta_{\text{naphthalene}} = 920$  ML and  $\Theta_{2\text{-methylbiphenyl}}$  of 142 ML. The first peak is the  $\lambda_{\text{max}} \sim 310$  nm seen in the neat 2-methylbiphenyl and the 2<sup>nd</sup> peak at  $\lambda_{\text{max}} \sim 321$  nm (arrow) can be seen at these high coverages of naphthalene. The naphthalene/2-methylbiphenyl complex is the intense peak at 204 K with  $\lambda_{\text{max}} \sim 326$  nm. Inset: top view.

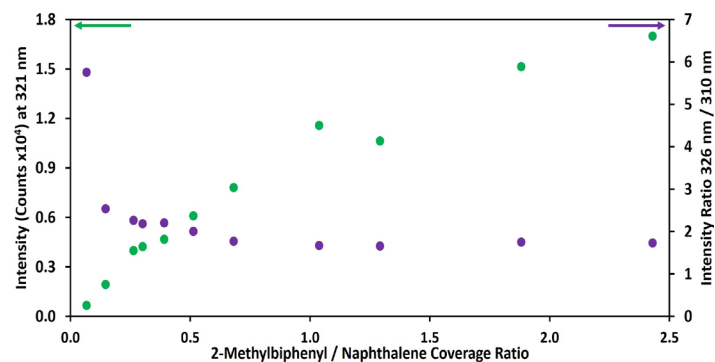
of the peak at 321 nm was evidence that epitaxy was driving the growth of this more planar 2-methylbiphenyl species and if deposition were continued, so will this peak's intensity.

As also seen in Figure 4, the most intense peak appeared at 204 K. It begins at 190 K and disappeared at desorption. Since this was present only in the bilayer (Cf. Figures 2 and 3) this fluorescence was tentatively attributed to a weakly held van der Waals complex composed of the two components in the excited state complex or exciplex. This was composed of two peaks at  $\lambda_{\text{max}} \sim 326$  and 336 nm. Since the intensities of these two peaks increased proportionately with coverage, the longer wavelength peak was assigned as a vibration built on the 326 nm peak. Based on the  $\lambda_{\text{max}}$  values, the dihedral angle for the complex is  $27^\circ$  which is  $10^\circ$  more planar than when it was epitaxially on naphthalene. The ratio of fluorescence intensities of the 326 nm to 310 nm was plotted as a function of the ratio of  $\Theta_{\text{naphthalene}}$  over  $\Theta_{2\text{-methylbiphenyl}}$  and is shown in Figure 5. Instead of just the fluorescent intensities of the 326 nm peak, the ratios were used to normalize the intensities due to the run-to-run variation in the coverages. The leveling in the plot shows that the exciplex composed of naphthalene and 2-methylbiphenyl interacted with a molecular ratio of roughly 1:1.

#### *2,2'-Dimethylbiphenyl adlayer and naphthalene/2,2'-dimethylbiphenyl bilayer:*

The wavelength-resolved TPD of 2,2'-dimethylbiphenyl multilayer (neat) at  $\Theta_{2,2'\text{-dimethylbiphenyl}} = 36$  ML is shown in Figure 6. The peak desorption temperature,  $T_p$ , was 228 K. First-order desorption was assumed and the activation energy for desorption,  $E_a$ , was calculated to be 58.9 kJ/mol.<sup>11-13</sup> Upon deposition, the fluorescence origin was at  $\lambda_{\text{max}} \sim 301$  nm and remained fixed throughout the TPD experiment. The dihedral angle from the trend line equation is  $87^\circ$ .

Shown in Figure 7 is the wavelength resolved TPD of the naphthalene and 2,2'-dimethylbiphenyl bilayer. As can be observed from both the angled view and the inset, there are two peaks in the initial spectra:  $\lambda_{\text{max}}$  at 301 and 312 nm. The first of these is also observed in the neat spectrum and therefore is assigned to the molecules that are not bound to the underlayer naphthalene.



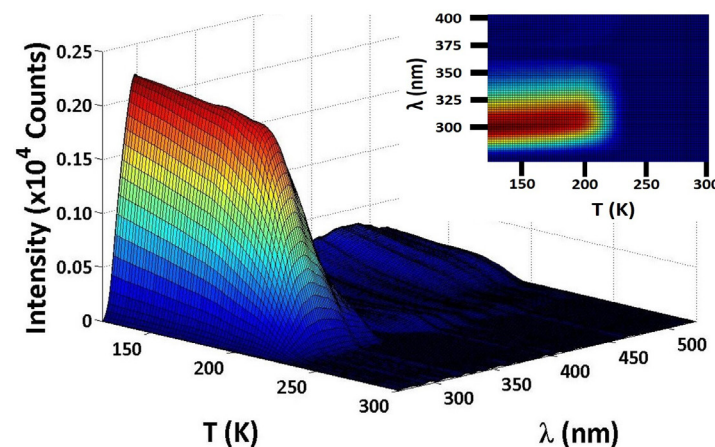
**Figure 5.** A plot of the fluorescence intensity at 321 nm at the deposition temperature of 115 K as a function of the ratio of  $\Theta_{2\text{-methylbiphenyl}}$  to  $\Theta_{\text{naphthalene}}$  (green plot, y-axis on left).  $\Theta_{\text{naphthalene}}$  was kept constant at  $74 \pm 14$  ML while  $\Theta_{2\text{-methylbiphenyl}}$  was varied. This indicates epitaxy.

A plot of the ratio of fluorescence intensities of the complex at 326 nm measured at 204 K and 310 nm at 115 K was plotted as a function of the ratio of  $\Theta_{\text{naphthalene}}$  and  $\Theta_{2\text{-methylbiphenyl}}$  (purple plot, y-axis on right).  $\Theta_{2\text{-methylbiphenyl}}$  was kept constant at  $128 \pm 18$  ML while  $\Theta_{\text{naphthalene}}$  was varied. This shows the stoichiometry of exciplex to be 1:1.

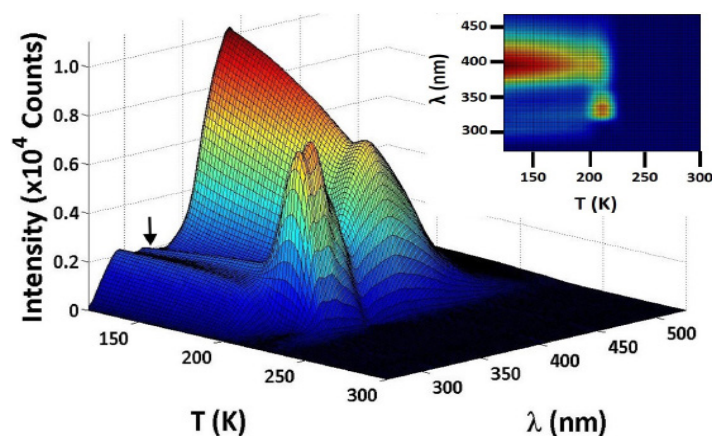
The second peak is assigned to those molecules that are epitaxially bound to the naphthalene underlayer. The resolvable  $\lambda_{\max}$ 's infer that the conformer of 2,2'-dimethylbiphenyl on naphthalene is discrete, rather than distributed over a range of dihedral angles. From the trend line in Figure 1, the torsional angles for 2,2'-dimethylbiphenyl were determined to be 87° and 58° for the 301 and 312 nm peaks, respectively.

A plot of the ratio of 312 nm / 301 nm intensities as a function of  $\Theta_{\text{naphthalene}} / \Theta_{2,2'\text{-dimethylbiphenyl}}$  is shown in Figure 8. The relative intensities leveled as the ratio of naphthalene to 2,2'-dimethylbiphenyl coverage was increased to about 1.0-1.5 ML/ML. The inference is that the interaction between naphthalene and 2,2'-dimethylbiphenyl occurred with this molecular composition.

During the TPD, two intense peaks with  $\lambda_{\max}$  = 324 and 334 nm appeared at 210 K as seen in Figure 7. As with 2-methylbiphenyl, the 334 nm peak that is separated by 10 nm from the 324 nm peak was assigned to a molecular vibration. From the trend line equation, the dihedral angle of the peak at 324 nm was 31°. The 2,2'-dimethylbiphenyl in the exciplex was more planar than the epitaxial conformer by 27°. This could mean that the complex was



**Figure 6.** Wavelength resolved TPD of  $\Theta_{2,2'\text{-dimethylbiphenyl}}$  of 36 ML of neat 2,2'-dimethylbiphenyl. Inset: top view. Note that the  $\lambda_{\max} \sim 301$  nm fluorescence is essentially constant through the entire TPD. Inset: top view.



**Figure 7.** Wavelength resolved TPD of bilayer of naphthalene and 2,2'-dimethylbiphenyl.  $\Theta_{\text{naphthalene}}$  was 183 ML and  $\Theta_{2,2'\text{-dimethylbiphenyl}}$  of 53 ML. The first peak at 301 nm is the same peak that is observed in neat 2,2'-dimethylbiphenyl as seen in Figure 6. The weak fluorescence with a  $\lambda_{\max} \sim 312$  nm is the species that is epitaxially associated with naphthalene (arrow). The naphthalene/2-methylbiphenyl complex is the intense peak at 210 K with  $\lambda_{\max} \sim 326$  nm. Inset: top view.

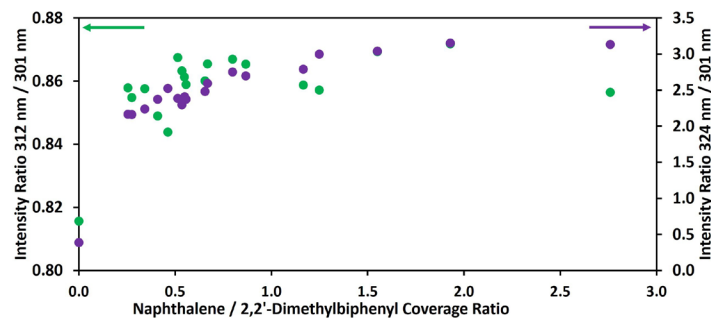
very tightly bound with a small intermolecular distance. A plot of the ratio of intensities of the 324 nm to 301 nm as a function of the ratio of 2,2'-dimethylbiphenyl to naphthalene coverages,  $\Theta_{\text{naphthalene}} / \Theta_{2,2'\text{-dimethylbiphenyl}}$  is shown in Figure 8. The leveling off occurred at about coverage ratio of 1.5-2 ML/ML and most likely represents the stoichiometric composition of the exciplex.

It should be noted that neither 2,2'-dimethylbiphenyl nor 2-methylbiphenyl exhibited the distinct disorder-to-order transition exhibited by other substituted biphenyl molecules. This was due to the steric hindrance at the ortho positions.

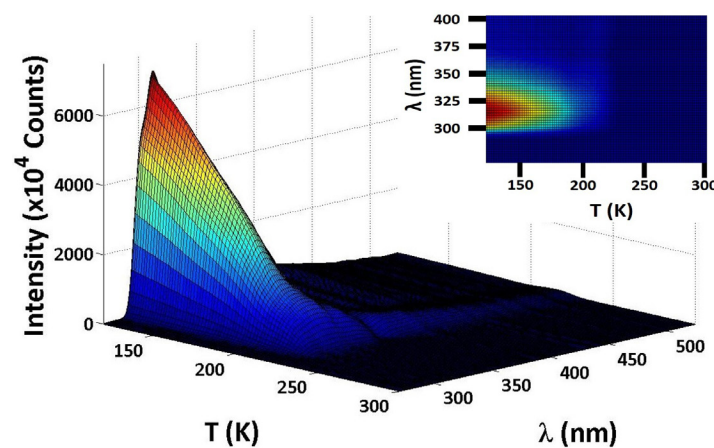
### 3-Methylbiphenyl multilayer:

The wavelength-resolved TPD of 3-methylbiphenyl is shown in Figure 9. The coverage of  $\Theta_{3\text{-methylbiphenyl}}$  was 108 ML. The fluorescence had a  $\lambda_{\max}$  of 314 nm that correlated to a dihedral angle of 53° from Figure 1. At about 200 K, 3-methylbiphenyl underwent a weak disorder-to-order transition, where the transition in which the intensity change was not as distinct compared to biphenyl. The desorption temperature,  $T_p$ , was 223 K and the calculated activation energy for desorption was 57.6 kJ mol<sup>-1</sup>.

In the bilayer study with naphthalene as the underlayer, the fluorescence had a  $\lambda_{\max}$  of 320 nm with a corresponding dihedral angle of 39° for 3-methylbiphenyl. This showed that 3-methylbiphenyl has the tendency to deviate from the initial dihedral angle by 14°. This was comparable to the behavior of biphenyl. In addition, when deposited on biphenyl that had been annealed at 170 K



**Figure 8.** A plot of the ratio of fluorescence intensities at 312 nm and 301 nm (green plot, y-axis on left) and the complex intensity ratio at 324 nm and 301 nm (purple plot, y-axis on right) as a function of the ratio of  $\Theta_{\text{naphthalene}}$  and  $\Theta_{2,2'\text{-dimethylbiphenyl}}$  was kept constant at  $49 \pm 6$  ML while  $\Theta_{\text{naphthalene}}$  was varied.



**Figure 9.** Wavelength resolved TPD of multilayer 3-methylbiphenyl.  $\Theta_{3\text{-methylbiphenyl}}$  of 108 ML. The peak at  $\lambda_{\max} \sim 314$  nm. Inset: top view.

which was past the disorder-to-order transition, the fluorescence  $\lambda_{\text{max}}$  red-shifted from  $\sim 314$  nm in the neat to 321 nm in the bilayer. The same wavelength shift was also observed when deposited on biphenyl that had been deposited at 138 K.

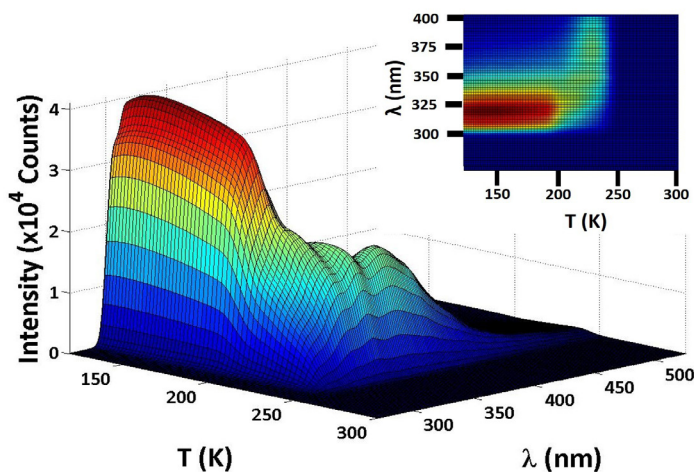
### 3,3'-Dimethylbiphenyl multilayer:

The wavelength-resolved TPD of 3,3'-dimethylbiphenyl with a coverage of approximately 200 ML is shown in Figure 10. The  $T_p$  was 238 K and the activation energy for desorption was calculated to be  $61.7 \text{ kJ mol}^{-1}$ . Upon deposition, a  $\lambda_{\text{max}}$  of 307.7 nm was observed, along with a more intense vibrational peak with a  $\lambda_{\text{max}}$  of 318 nm. The disorder-to-order transition was observed at 200 K, with a red-shift of the  $\lambda_{\text{max}}$  to 345 nm (black arrow in Figure 10). At approximately 226 K, a broad, featureless peak with a  $\lambda_{\text{max}}$  of 370 nm was detected, which has been assigned as the excimer of 3,3'-dimethylbiphenyl (green arrow in Figure 10).

An epitaxial study was done with naphthalene as the underlayer and no shift in the  $\lambda_{\text{max}}$  of was detected. A complex appeared to form at about 202 K, with a  $\lambda_{\text{max}}$  of 324 nm, along with the vibrational  $\lambda_{\text{max}}$  at 333 nm. Here again, the 333 nm peak was more intense than the 324 nm fluorescence. When biphenyl that had been deposited at 138 K or annealed to 170 K as underlayers, 3,3-dimethylbiphenyl did not show evidence of epitaxial growth on these two planar forms of biphenyl.

### 4-Methylbiphenyl multilayer:

The wavelength-resolved TPD of 4-methylbiphenyl that had been vapor deposited with a coverage of  $\Theta_{4\text{-methylbiphenyl}}$  of 188 ML is shown in Figure 11. The peak desorption temperature was 236 K. First-order desorption was assumed and the activation energy for desorption,  $E_a$ , was calculated to be  $61.3 \text{ kJ mol}^{-1}$ . As can be seen from Figure 11, the  $\lambda_{\text{max}}$  of the fluorescence which is at 321 nm upon deposition remains constant through the TPD. Theoretically calculated angle<sup>6</sup> of  $42^\circ$  agree well with the dihedral angle of  $37^\circ$  as determined from the trend line given in Figure 1. A narrowing of the peak width was observed at 150 K, presumably from the reorganization of the molecules as the thermal energy was increased and the adlayer underwent an annealing process.

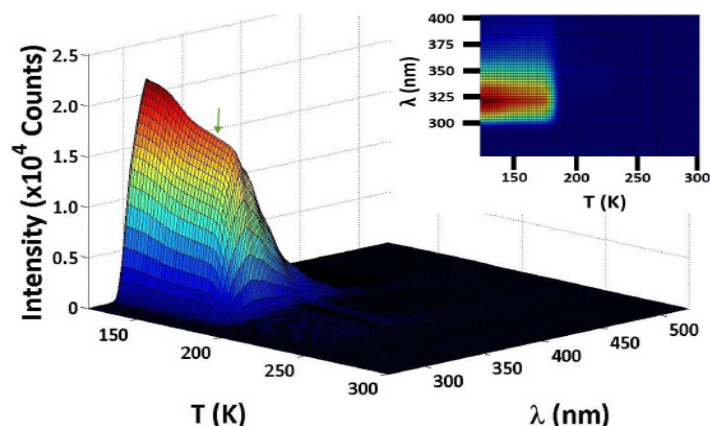


**Figure 10.** Wavelength-resolved TPD of 3,3'-dimethylbiphenyl with  $\Theta_{3,3\text{-dimethylbiphenyl}} = 200$  ML. Deposition was at 115 K. At 200 K, a peak appears with  $\lambda_{\text{max}}$  at 345 nm (black arrow) which is due to disorder-to-order transition with  $\lambda_{\text{max}}$  at 345 nm and at 370 nm (green arrow) due to excimer formation. Inset: top view.

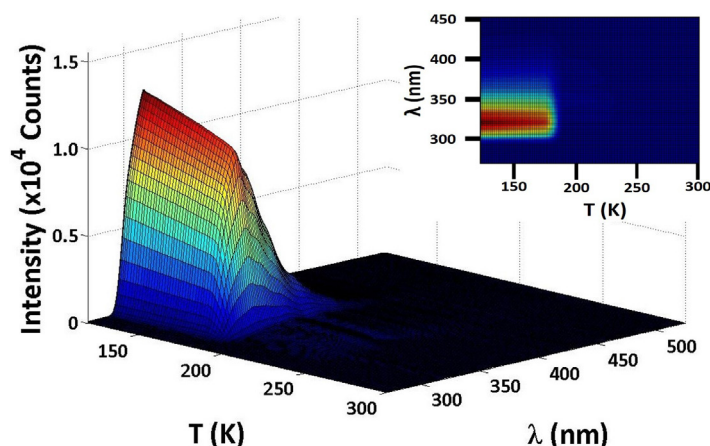
During a 10 K interval beginning at 172 K the adlayer underwent a disorder-to-order process that was analogous to the behavior biphenyl. The process was associated with the almost complete quenching of the fluorescence. Although not shown here, the intensity of the transmitted excitation light was plotted as a function of temperature. The plot showed that the transmittance increased subsequent to the disorder-to-order transition. This would be the result expected of a more transparent adlayer when the transition to an ordered adlayer occurred and was consistent with a disorder-to-order transition.

Figure 12 shows the effect of annealing to 170 K, which is just short of the disorder-to-order transition. This caused the fluorescence intensity to fall linearly with increasing temperature due to thermally induced relaxation processes. In addition, annealing had the effect of narrowing the width of the peak at 321 nm while still exhibiting a disorder-to-order transition at the same temperature as without the anneal as shown in Figure 11.

When the deposition was performed at 130 K instead of 115 K as in Figure 11, a very different wavelength-resolved TPD was observed and is shown in Figure 13. Here two peaks were measured: one at a  $\lambda_{\text{max}}$  of 352 nm and another at 372 nm. From the trend line



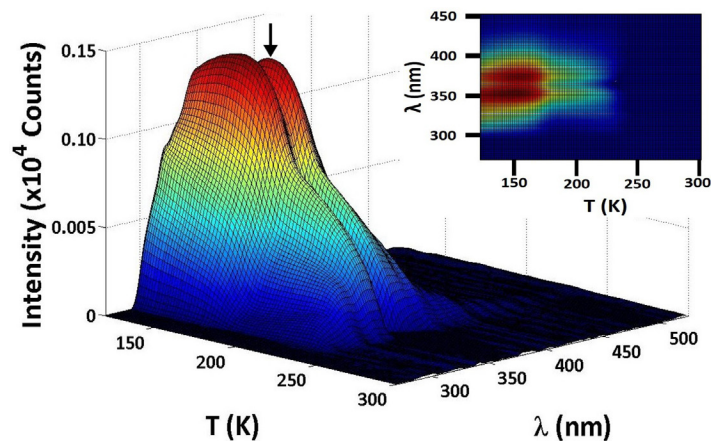
**Figure 11.** Wavelength-resolved TPD of 4-methylbiphenyl with  $\Theta_{4\text{-methylbiphenyl}} = 188$  ML. Deposition was at 115 K. Arrow points to the narrowing of the spectrum at 150 K. Inset: top view.



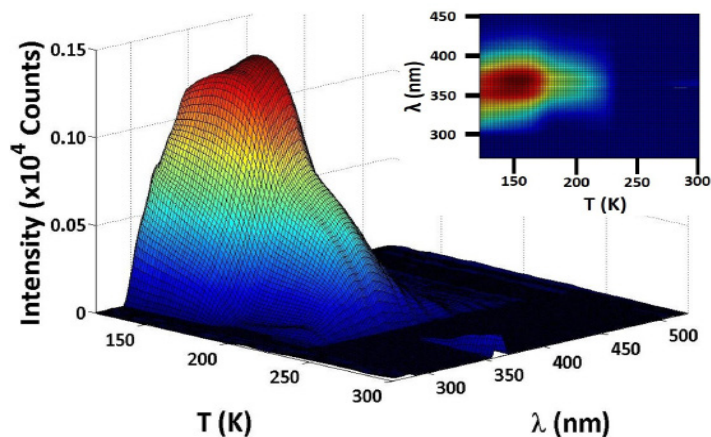
**Figure 12.** Wavelength-resolved TPD of 4-methylbiphenyl with  $\Theta_{4\text{-methylbiphenyl}} = 158$  ML that had been annealed at 170 K for 5 seconds. Inset: top view.

equation in Figure 1, the 352 nm peak corresponded to a  $0^\circ$  dihedral angle, and represented 4-methylbiphenyl molecules that were planar on  $\text{Al}_2\text{O}_3$ . The conclusion was that sufficient thermal energy existed at this surface temperature to cause the 4-methylbiphenyl to become ordered immediately upon deposition. This peak at 352 nm is qualitatively more narrow than the peak at 321 nm that was observed at deposition at 115 K.

Indicated by an arrow in Figure 13, the second peak at 372 nm is tentatively attributed to the excimer of 4-methylbiphenyl. Three reasons support this assignment. First, the  $\lambda_{\text{max}}$  of 372 nm for 4-methylbiphenyl was close to the  $\lambda_{\text{max}}$  of 370 nm of the excimer of biphenyl. Second, the broad spectrum that was observed here is characteristic of excimers.<sup>5</sup> Third, from Figure 1, the dihedral angle with this  $\lambda_{\text{max}}$  exceeded that of the planar molecule, 9,10-dihydrophenanthrene. We believe this is the first reported excimer of 4-methylbiphenyl. When the 352 nm spectrum was subtracted from the complete wavelength-resolved TPD as shown in Figure 14, what remains was the wavelength-resolved TPD of the 4-methylbiphenyl excimer. In the inset, the spectrally broad feature that is characteristic of excimer fluorescence is clearly evident.



**Figure 13.** Wavelength-resolved TPD of 4-methylbiphenyl in which the deposition was at 130 K. Two peaks at 352 nm and 372 (arrow) nm are observed.  $\Theta_{4\text{-methylbiphenyl}} = 160$  ML. Inset: top view.



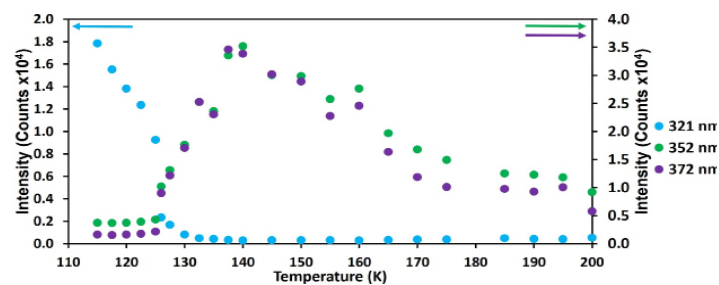
**Figure 14.** Wavelength-resolved TPD of 4-methylbiphenyl from Figure 13 in which the 352 nm peak has been subtracted out which emphasizes the 372 nm peak that has been assigned to the excimer of 4-methylbiphenyl. More specifically, the spectrum at 231.5 K in Figure 13 was subtracted from the entire TPD. Inset: top view.

Since the deposition temperature determined the species of 4-methylbiphenyl that form on  $\text{Al}_2\text{O}_3$ , in Figure 15, the fluorescence intensities at 321 nm (blue plot, y-axis to the left), 352 nm (green plot, y-axis to the right), and 372 nm (purple plot, y-axis to the right) were plotted as a function of the deposition temperature. When the intensity of the 321 nm peak (4-methylbiphenyl with a dihedral angle of  $37^\circ$ ) decreased to almost zero at a deposition temperature of 130 K, the 352 nm (planar) and 372 nm (excimer) peaks increased to maximum at  $\sim 140$  K as seen in the figure. These plots show that the presence of the planar conformer allowed for the formation of the excimer. Both intensities decrease after the disorder-to-order transition at 175 K (See Figure 15) until desorption at 236 K when they decreased to zero.

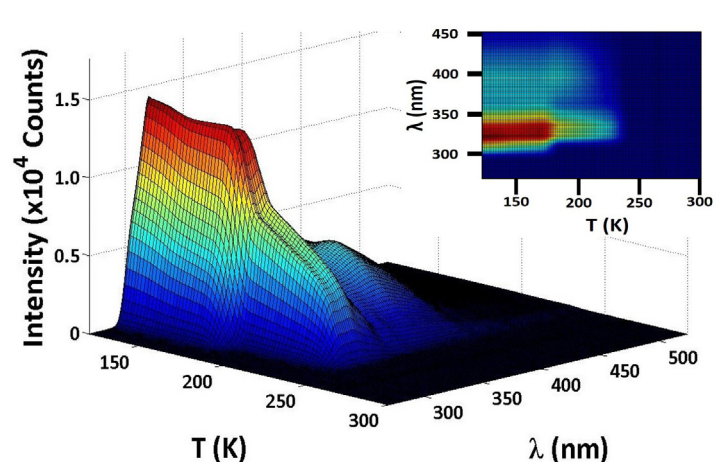
Three bilayer studies were done to understand the behavior of 4-methylbiphenyl when it was deposited on other molecules, such as naphthalene and biphenyl. These are described next.

#### *Bilayers of naphthalene/4-methylbiphenyl and biphenyl/4-methylbiphenyl:*

In previous epitaxy studies, the conformer of biphenyl was found to be fairly sensitive to the nature of the underlayer molecule.<sup>3-4</sup> For example when naphthalene was the underlayer, biphenyl readily became planar upon deposition on it.<sup>3-4</sup> When 4-methylbiphenyl was deposited on naphthalene, however, it did not deposit in the planar conformer, and rather it remained twisted as evidenced by the 321 nm fluorescence as seen in Figure 16. Furthermore, intermolecular interaction is presumed to be relatively weak in this case because naphthalene was found to desorb



**Figure 15.** Plot of the fluorescence intensity with  $\lambda_{\text{max}} \sim 321, 352$  and  $372$  nm as a function of the deposition temperature ( $\pm 1$ K).  $\Theta_{4\text{-methylbiphenyl}} = 176 \pm 11$  ML.



**Figure 16.** 4-Methylbiphenyl does not deposit in the planar conformer with naphthalene as the underlayer.  $\Theta_{\text{naphthalene}}$  was deposited with 67 ML and  $\Theta_{4\text{-methylbiphenyl}}$  was 189 ML. Note that the 321 nm peak is present and the 352 peak is absent. The 398 nm that is weakly present is the naphthalene excimer. Inset: top view

separately and at a lower temperature than 4-methylbiphenyl.

Biphenyl undergoes the disorder-to-order transition at about 160 K, whereupon it becomes more planar with the dihedral angle decreasing from  $41^\circ$  to  $25^\circ$ . When 4-methylbiphenyl was deposited on biphenyl that had been annealed at 170 K, so that the biphenyl underlayer was more planar, then 4-methylbiphenyl deposited in the most planar conformation ( $\lambda_{\max} = 352$  nm) (See Figure 17). In addition, the excimer was also present.

When biphenyl was deposited at 138 K, it was mostly in the planar conformer, but sufficiently amorphous that allowed for the formation of excimers.<sup>5</sup> When 4-methylbiphenyl was then deposited upon this underlayer of biphenyl, it also formed excimers with  $\lambda_{\max}$  of 372 nm, along with the planar conformer with  $\lambda_{\max}$  of 352 nm as shown in Figure 18. Noteworthy was that in both Figures 17 and 18, biphenyl, that normally desorbed at 227 K,<sup>5</sup> desorbed with the 4-methylbiphenyl. This was indicative of the high degree of van der Waals association for these two molecules.

#### 4,4'-Dimethylbiphenyl multilayer:

The wavelength-resolved TPD of 4,4'-dimethylbiphenyl that had been vapor deposited with a coverage of  $\Theta_{4,4'\text{-dimethylbiphenyl}}$  of

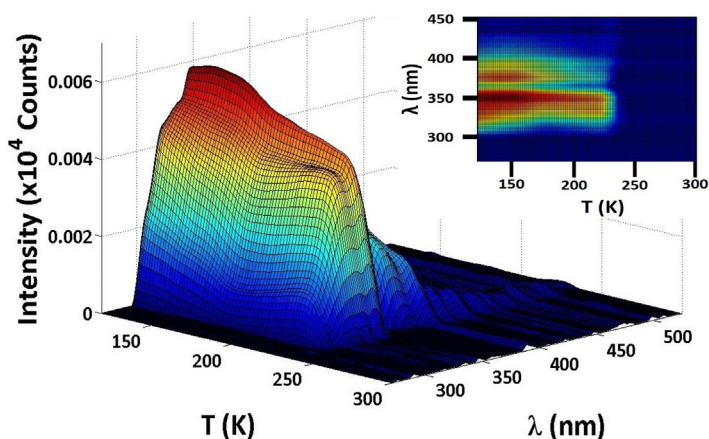


Figure 17. 4-Methylbiphenyl that had been deposited on biphenyl that had been annealed at 170 K to form the more planar biphenyl.  $\Theta_{\text{biphenyl}}$  was 79 ML and  $\Theta_{4\text{-methylbiphenyl}}$  was 117 ML. Inset: top view

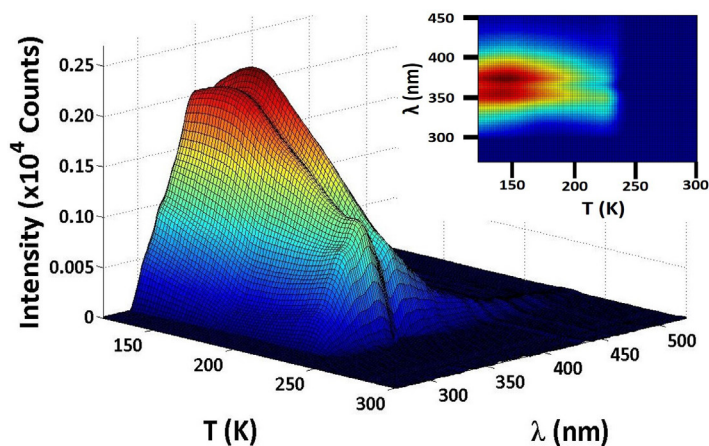


Figure 18. 4-Methylbiphenyl that had been deposited on biphenyl that had been deposited at 138 K to form the excimer.  $\Theta_{\text{biphenyl}}$  was 119 ML and  $\Theta_{4\text{-methylbiphenyl}}$  was 171 ML. The peaks at 352 nm and 372 nm are from the planar conformer and the 372 peak is from the excimer. Inset: top view.

117 ML is shown in Figure 19. The peak desorption temperature was 255 K. First-order desorption was assumed and the activation energy for desorption,  $E_a$ , was calculated to be  $65.4$  kJ mol<sup>-1</sup>. As can be seen from the inset to the figure, the  $\lambda_{\max}$  of the fluorescence which was at 324 nm upon deposition remained constant throughout the TPD. The trendline equation in Figure 1 gave a dihedral angle of  $31^\circ$  for this molecule. Possible disorder-to-order transition occurred at 200 K, but without change in the  $\lambda_{\max}$ .

Attempts were made to epitaxially cause 4,4'-dimethylbiphenyl to become more planar by deposition on the more planar conformer of biphenyl. The more planar conformers of biphenyl were formed by deposition at 138 K and 170 K that favored the formation of planar excimer and ordered biphenyl, respectively. In both cases, the  $\lambda_{\max}$  of 4,4'-dimethylbiphenyl did not change from 324 nm.

When 4,4'-dimethylbiphenyl was deposited on naphthalene, an intense peak occurred at 220 K, with  $\lambda_{\max}$  of 324 nm, as shown in Figure 20. A plot of the intensity of this peak (blue arrow), normalized against the intensity of this peak at deposition temperature of 120 K (green arrow) as a function of the ratio of coverages of naphthalene and 4,4'-dimethylbiphenyl,  $\Theta_{\text{naphthalene}}/\Theta_{4,4'\text{-dimethylbiphenyl}}$ , is shown in Figure 21. The leveling of the plot

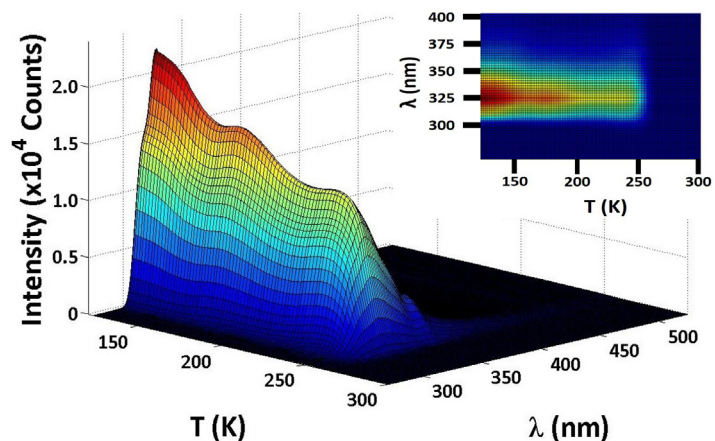


Figure 19. Wavelength resolved TPD of 4,4'-dimethylbiphenyl.  $\Theta_{4,4'\text{-dimethylbiphenyl}} = 117$  ML. Inset: top view

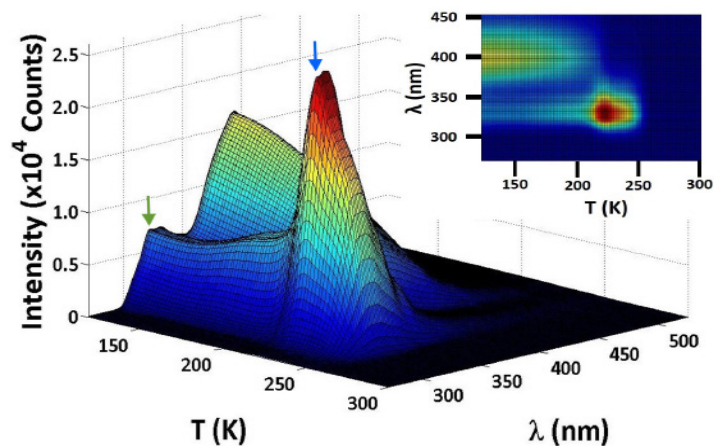
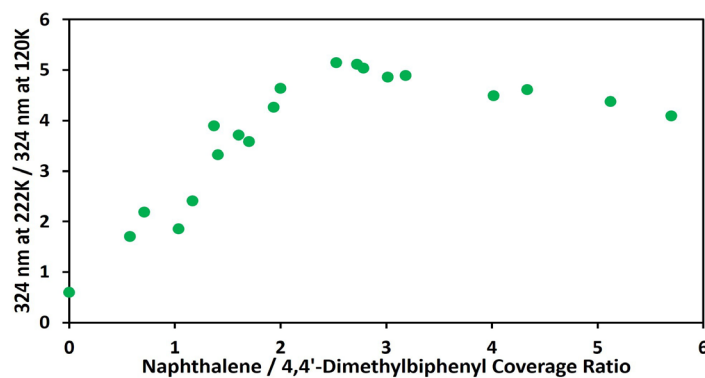


Figure 20. Wavelength resolved TPD of naphthalene/4,4'-dimethylbiphenyl bilayer.  $\Theta_{\text{naphthalene}} = 93$  ML, and  $\Theta_{4,4'\text{-dimethylbiphenyl}} = 58$  ML. Blue arrow points to the 324 nm exciplex fluorescence at 222 K and the green arrow, at the fluorescence at 324 nm upon deposition. The peak at 398 nm is the naphthalene excimer. Inset: top view

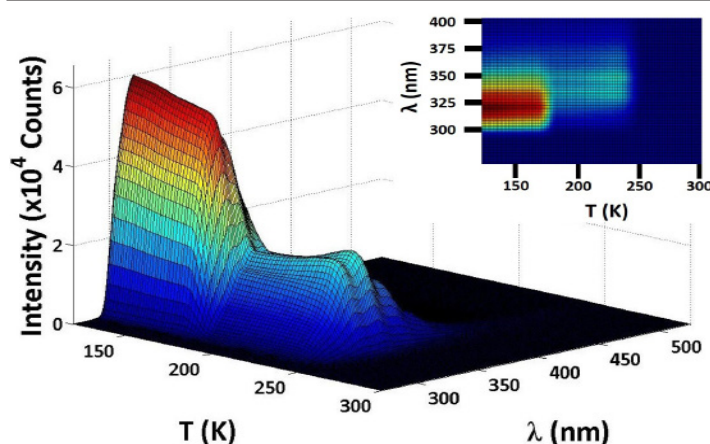
at a coverage ratio of 2:1 naphthalene/4,4'-dimethylbiphenyl gave the approximate stoichiometry of the van der Waals complex. It should be noted that 4,4'-dimethylbiphenyl did not epitaxially form on naphthalene as indicated by the  $\lambda_{\max}$  that did not change when deposited on naphthalene underlayer.

#### 4-Ethylbiphenyl multilayer:

The wavelength-resolved TPD of vapor deposited 4-ethylbiphenyl on  $\text{Al}_2\text{O}_3$  with a  $\Theta_{4\text{-ethylbiphenyl}}$  of 107 ML is shown in Figure 22. The peak desorption temperature,  $T_p$ , for lower coverages was 240 K, and the  $E_a$  was calculated to be 61.4 kJ mol<sup>-1</sup>. Three  $\lambda_{\max}$ 's at 322, 349 and 369 nm were observed. The peak at 322 nm was 4-ethylbiphenyl with a dihedral angle of 35° as determined from the equation in Figure 1, This would be the twisted conformer of the amorphous adlayer molecules. The second peak at 349 nm was observed after the disorder-to-order transition which was at 180 K and was due to the planar conformer. with a dihedral angle of 0°. The third peak at 369 nm was most likely due to the excimer fluorescence, analogously to biphenyl and 4-methylbiphenyl. The intensities of these peaks as a function of deposition temperatures are plotted in Figure 23. The intensity of the 322 nm peak decreased at 130 K with a concomitant increase in intensities of the 349 and 369 nm peaks. The optimum temperature for the formation of the 4-ethylbiphenyl excimer was



**Figure 21.** Plot of the ratio of the intensities at 222 K at 324 nm (blue arrow in Figure 20) and at 120 K (green arrow in Figure 20) as a function of the ratio of coverages of naphthalene in ML and 4,4'-dimethylbiphenyl. The coverage of naphthalene was varied while  $\Theta_{4,4'\text{-dimethylbiphenyl}}$  was held constant at  $62 \pm 7$  ML.

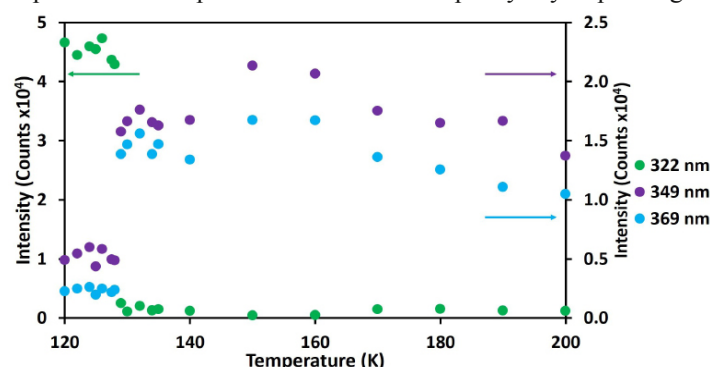


**Figure 22.** Wavelength resolved TPD of 4-ethylbiphenyl.  $\Theta_{4\text{-ethylbiphenyl}} = 107$  ML. Initially,  $\lambda_{\max}$  is 322 nm. The disorder-to-order transition is at 180 K, and the red-shifted fluorescence with  $\lambda_{\max}$  of 349 and 369 nm were observed with much lower intensities. Inset: top view. All three wavelengths are clearly visible.

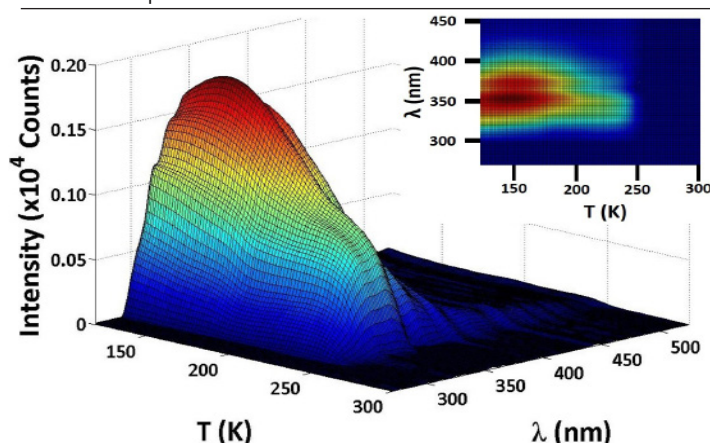
determined to be 150 K.

The wavelength-resolved TPD for 4-ethylbiphenyl that had been deposited at 150 K is shown in Figure 24. As can be clearly seen in the inset, the 349 nm peak was present, along with the broader fluorescence at 369 nm. Both of these fluorescence emissions are from the planar conformers of 4-ethylbiphenyl, with the latter being attributed to the excimer.

In the bilayer experiments, 4-ethylbiphenyl did not complex with naphthalene, nor did it epitaxially become more planar when deposited on naphthalene. In addition, when 4-ethylbiphenyl was deposited on the planar conformers of biphenyl by depositing at



**Figure 23.** Plot of the absolute intensities of the three  $\lambda_{\max}$  of interest: 322 nm due to the twisted conformer, 349 nm due to the planar and 369 nm due to the excimer of 4-ethylbiphenyl as a function of the deposition temperature.  $\Theta_{4\text{-ethylbiphenyl}} = 86 \pm 23$  ML. At about 130 K, the 322 nm peak decreases with a concomitant increase in the other two peaks' intensities.



**Figure 24.** Wavelength resolved TPD of 4-ethylbiphenyl that was deposited at 150 K.  $\Theta_{4\text{-ethylbiphenyl}} = 68$  ML. The fluorescence with  $\lambda_{\max}$  of 349 and 369 nm are observed. Inset: top view.

**Table 1.** Dihedral angles (in °) and  $\lambda_{\max}$  (nm in parentheses) of biphenyl molecules at deposition, the disorder-to-order transition (temperatures in parentheses), epitaxy with naphthalene underlayer, exciplex (excited state complex) with naphthalene and excimers.

	angle at deposition (λ(nm))	disorder-order transition (λ(nm), T(K))	epitaxy on naphthalene (λ(nm))	exciplex naphthalene (λ(nm))	excimer (λ(nm), T(K))
biphenyl	41° (319nm) <sup>3</sup>	25°(327nm,160K) <sup>2</sup>	29° (325nm) <sup>14</sup>	29° (325nm) <sup>14</sup>	3°(370nm,138K) <sup>5</sup>
2-methylbiphenyl	63° (310nm)	-	37° (321nm)	27° (326nm)	-
2,2'-dimethylbiphenyl	87° (301nm)	-	58° (312nm)	31° (324nm)	-
3-methylbiphenyl	53° (314nm)	37°(321nm,200K)	39° (320nm) <sup>a</sup>	-	-
3,3'-dimethylbiphenyl	68° (308 nm)	1° (345nm,200K)	-	15° (333nm)	0°(370nm,226K)
4-methylbiphenyl	37° (321nm)	0°(352nm,175K)	0° (352nm) <sup>b</sup>	-	0°(372nm,130K) <sup>c</sup>
4,4'-dimethylbiphenyl	31° (324nm)	31°(324nm,200 K)	-	31° (324nm)	-
4-ethylbiphenyl	35° (322nm)	0°(349nm,180 K)	-	-	0°(369nm,150K) <sup>c</sup>

- = did not observe

<sup>a</sup>epitaxial also with planar and excimer biphenyl underlayer 37°(321nm)

<sup>b</sup>epitaxial with planar and excimer of biphenyl 0°(352nm)

<sup>c</sup>excimer newly reported



138 K to form the excimer or by annealing to 170 beyond the disorder-to-order transition, its fluorescence did not red-shift from the 322 nm. The conclusion was that the extra floppiness due to the added methylene group did not allow for it to interact as strongly as 4-methylbiphenyl did with either biphenyl or naphthalene.

In summary:

The results are summarized in Table 1. From these changes in the biphenyl group's torsional angle when epitaxially deposited on naphthalene and when complexed with naphthalene, the rotational energy barrier appears low. Van der Waals energies are of the order of a few kJ/mol. Since calculations show that the rotational barriers are about 7 kJ mol<sup>-1</sup> for biphenyl, 50 kJ mol<sup>-1</sup> for 2-methylbiphenyl and > 100 kJ mol<sup>-1</sup> for 2,2'-dimethylbiphenyl,<sup>6,10</sup> perhaps the rotational barriers are steeply inclined when closer to 0°, but flatter otherwise. Some rotational barrier calculation seem to indicate this<sup>6,10</sup> and this study appears to provide experimental evidence to support these calculations.

Although actual structures of the complexes must await further studies by computation and/or experiment, it is encouraging that additional insight as to the dihedral angles that these biphenyl molecules have in different environments can be obtained by this method. The hope is to add other biphenyl molecules to this list to increase the precision of the torsional angles in relation to their spectra.

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## References

1. A. Almenningen, O. Bastiansen, L. Fernholt, B.N. Cyvin, S.J. Cyvin and S. Samdal. *J. Mol. Struct.*, **1985**, 128, 59-76.
2. G.P. Charbonneau and Y. Delugeard. *Acta Crystallographica B*, **1976**, 32, 1420-1423.
3. M.K. Condie, Z.E. Moreau and A.M. Nishimura. *J. Undergrad. Chem. Res.*, **2019**, 18, 15-18.
4. B.D. Fonda, M.K. Condi, Z.E. Moreau, Z.I. Shih, B. Dionisio, A. Fitts, L. Foltz, K. Nili and A.M. Nishimura. *J. Phys. Chem. C.*, **2019**, 123, 26185-26190.
5. M.K. Condie, C. Kim, Z.E. Moreau, B. Dionisio, K. Nili, J. Francis, C. Tran, S. Nakaoka and A.M. Nishimura. *J. Undergrad. Chem. Res.*, **2020**, 19, 14-17.
6. F. Grein, *J. Phys. Chem. A*, **2002**, 106, 3823-3827.
7. H. Cileau, A. Girard, F. Moussa, and C.M.E. Zeyen, *Solid State Comm.* **1979**, 29, 259
8. R. Cosmo, T.W. Hambley, and S. Sternhell, *J. Org. Chem.*, **1987**, 14, 3119-3123.
9. G.M Brown and M.H. Bortner, *Acta Cryst.*, **1954**, 7, 139,
10. A.J. Grumadas, D.P. Poshkus, and A.V. Kiselev, *J. Chem. Soc. Faraday Trans.*, **1982**, 78, 2013-2023.
11. P.A. Redhead. *Vacuum*, **1962**, 12, 203-211.
12. F.M. Lord, J.S. Kittelberger. *Surf. Sci.*, **1974**, 43, 173-182.
13. D.A. King. *Surf. Sci.*, **1975**, 47, 384-402.
14. S.C. Rosenhagen, C.C. Tran and A.M. Nishimura, *J. Under-*