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ENHANCED BIPHENYL TRAP FLUORESCENCE CAUSED BY 1,6-DICHLOROHEXANE ON Al_2O_3

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Abstract

Fluorescence of biphenyl was used to monitor its surface dynamics when vapor deposited on Al_2O_3. For example, upon deposition, biphenyl is initially amorphous, but undergo disorder-to-order transition when the temperature of the substrate is ramped during the temperature programmed desorption (TPD) experiment. When biphenyl is an overlayer in a bilayer with 1,6-dichlorohexane as the underlayer, a large increase in the fluorescence was observed when the latter percolated through the biphenyl layer as it desorbed. The cause has been attributed to a strong intermolecular interaction between the chlorine and the π electrons that disrupted the order in the biphenyl adlayer and separated the fluorophores so that self-emission was the dominant relaxation pathway.

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Keywords: biphenyl, 1,6-dichlorohexane, adsorption, vapor deposition, desorption, temperature programmed desorption, TPD

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Introduction

In a recent study, biphenyl was used as a probe to characterize the surface morphology of the adlayer that it formed when1-chloroalkanes and dichloroalkanes were vapor deposited on an Al_2O_3 surface.[1,2] Due to dispersion forces, the alkyl chain organized to form adsorption sites if the length of the alkyl moiety was sufficient to accommodate the fluorophore.[3-6] In these studies, biphenyl exhibited the largest increase in its fluorescence intensity with one underlayer molecule in particular, 1,6-dichlorohexane. When this underlayer molecule percolated through the biphenyl adlayer, the intensity of the biphenyl fluorescence increased as much as 2.25 times what was observed before the temperature was ramped. The purpose of this study was to better understand the how and why of this observation.

Experimental

Biphenyl, 1,8-dichlorooctane, 1,6-dichlorohexane, 1,5-dichlorohexane, 1,4-dichlorobutane, 1,3-dichloropropane, 1,2-dichloroethane, dichloromethane and hexane were of the highest purity (> 99%) that could be purchased from commercial sources (Sigma-Aldrich, St. Louis, MO). They were placed in a sample holder attached to one end of a precision leak valve for vapor deposition. The ultra-high vacuum chamber had a background hydrogen base pressure of 1 x 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. Resistive heating of the Al_2O_3 was done by sending current through a thin tantalum foil that was in thermal contact with the substrate. 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.

The biphenyl in the adlayer was optically pumped with a high pressure mercury lamp and the wavelength selected at 250 nm using a 0.25 m monochromator. During the TPD, the LabVIEW program also took the fluorescence spectra every 300 ms in real time from an Ocean Optics USB4000 spectrometer (Ocean Optics, Dunedin, FL) that was sensitive in the ultra-violet (UV). Manipulation of the array of spectra as a function of temperature by a MATLAB (Mathworks, Natick, MA) template yielded the WRTPD's (wavelength resolved TPD) 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.[7]

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 is based on the mass spectral peak desorption temperature, T_p.[8-10] The uncertainties in the desorption temperatures lead to a propagated error in the activation energies of ± 2%, unless otherwise stated.

The LabVIEW coded program also was run on a computer that received data from a residual gas analyzer so that both the deposition and the desorption of biphenyl and the other adsorbates could be monitored. The surface coverages, Θ, in monolayers (ML) were calculated by calibrating the integrated mass spectral peaks to an optical interference experiment.[7-8] The interference experiment yielded accurate rate of deposition with coverage error of ± 30%, and is described in detail elsewhere.[7-8]

Transmittance of the excitation light was detected with a photomultiplier was connected to a computer interfaced high resolution analog-to-digital converter that the same LabVIEW program controlled. A UV shortpass optical filter had been placed in front of the photomultiplier detector so that only the 250 nm excitation light was being monitored. The voltages from the photomultiplier at 0% and 100% transmittances were determined by first blocking the excitation light and then using same optical configuration with a clean surface, respectively. In this way, the transmittance correlated linearly with the voltages from the photomultiplier.

A pulsed quadrupled Nd:YAG laser with output at 266 nm was the excitation source for the laser-induced fluorescence, LIF, measurements. The fluorescence was focused with short focal length lens onto a 0.25 m monochromator equipped with a photomultiplier and λ_0 was set at 340 nm, the peak of the biphenyl fluorescence. The signal from the photomultiplier was amplified and sent to a very fast digitizing oscilloscope, averaged over 4 scans and the waveform was exported to the controlling computer that was running the LabVIEW program. The LIF was assumed to decay by first-order kinetics. A least square curve-fitting program was used to determine the slope, i.e. the rate constant, and intercept of this line during the TPD experiment. The intercepts are the initial intensities of the LIF decay. About 6 replicates of TPD runs yielded LIF decay rate constants with a precision of about ± 10%.

Previously a correlation between the biphenyl's dihedral angle and its fluorescence λ_{max}, was determined in a study of 11 biphenyl molecular species with 2,2'dimethylbiphenyl on one extreme with a dihedral angle of 90º and 9,10-dihydrophenanthrene with a dihedral angle of 0º were plotted.[12] The trendline equation was a second-order polynomial which was then used to calculate a dihedral angle to biphenyl compound from the λ_{max} of biphenyl compound in any molecular environment.[12] The error in the dihedral angle has been estimated to be around ± 10%.[12]

The enhanced biphenyl fluorescence depended upon the morphology of the underlayer.[1,2] More specifically, if the underlayer were annealed, some ordering occurred and this in turn caused the biphenyl fluorescence intensity to exhibit the maximum effect. For 1,6-dichlorohexane, the optimum annealing temperature was determined to be 130 K.[1] This annealing temperature was used in all subsequent experiments.

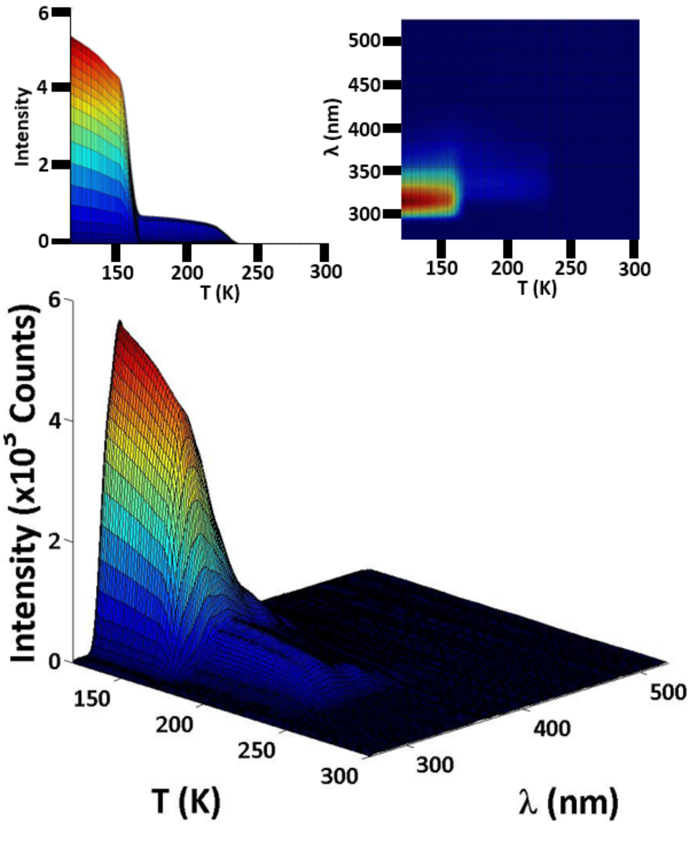

Figure 1. Wavelength-resolved TPD of biphenyl with a λ_{max} at 318 nm. The disorder-to-order transition occurred at about 160 K and λ_{max} red-shifted to 338 nm. $\Theta_{biphenyl}$ ~ 97 ML. Left Inset: side view. Right Inset: top view.

Results and Discussion

The arrangement of biphenyl molecules in the vapor deposited adlayer was amorphous and disordered, [1,2,7,12] with a λ_{max} at 318 nm. As described in the experimental section, the dihedral angle of the biphenyl at this wavelength was calculated to be 41 ± 4º.[12] At 160 K during the TPD, the adlayer underwent a transition from disorder to a more ordered arrangement. This can be seen in Figure 1. In this ordered arrangement, the resonant energy transfer pathway competes with the radiative relaxation and quenches the fluorescence. In this arrangement, λ_{max} red-shifted to 338 nm and the dihedral angle at this wavelength was calculated to be ~4º.[12]

In previous studies, fluorophores were used to probe the morphological changes that occur during TPD procedures on these bimolecular adlayers on Al_2O_3.[1,2] The peak desorption temperature, T_p, of neat biphenyl at low coverages was 229 K. First-order desorption was assumed and the activation energy for desorption, E_a, was calculated to be 60 kJ/mol.[8-10]

Biphenyl/1,6-Dichlorohexane

The spectral signatures of biphenyl remained the same in the bilayer with 1,6-dichlorohexane as the underlayer. Upon deposition and the start of the TPD, the λ_{max} was the same as in the neat biphenyl. The disorder-to-order transition was also accompanied by the red-shift to a doublet at 332 nm and 342 nm. Tentatively this doublet has been assigned to a C-C stretching vibration. The 0,0

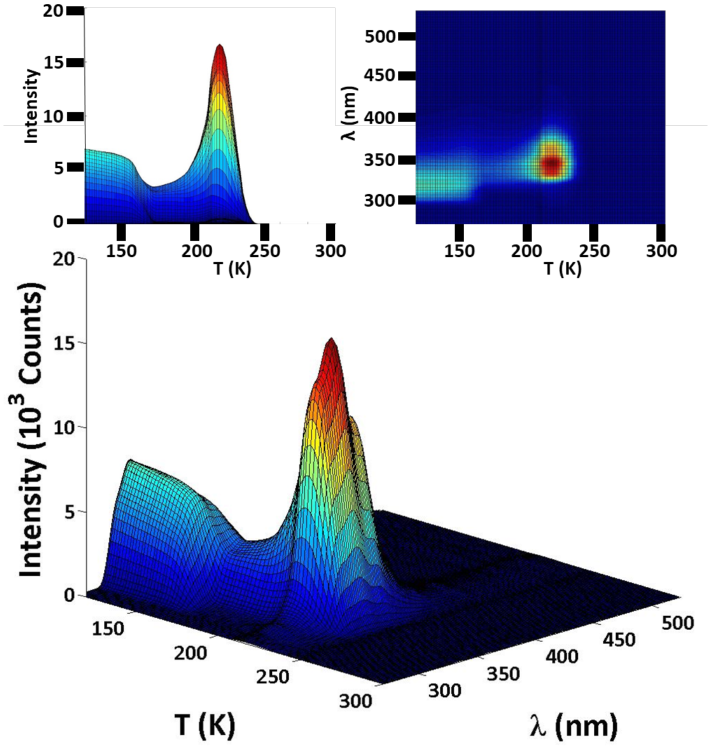

Figure 2. Wavelength-resolved TPD of a bilayer of 1,6-dichlorohexane and biphenyl with $\Theta_{1,6\text{-dichlorphexane}}$ ~ 108 ML with a overlayer of $\Theta_{biphenyl}$ ~ 102 ML During the TPD, the twisted conformer with λ_{max} of 318 nm dominate at deposition up to 160 K. This conformer underwent disorder-to-order transition at 160 K and the trap fluorescence at 218 K appeared as a doublet with λ_{max} of 332 nm and 342 nm the intensity of which was dependent on the $\Theta_{1,6\text{-dichlorohexane}}$ coverage. Left and right insets: side and top views, respectively.

transitional wavelength of 332 nm correspond to dihedral angle of 15º for the conformer of biphenyl from which the fluorescence originated.[1,2]

1,6-Dichlorohexane desorbs with a T_p of 211 K and if first-order desorption was assumed, the activation energy for desorption, E_a, was calculated to be 55 kJ/mol.[8-10] Since 1,6-dichlorohexane has a lower desorption temperature than biphenyl, the underlayer molecules percolated through the overlayer before it desorbed during the TPD procedure.[1] *Subsequent* to and during desorption, the biphenyl trap intensity was observed to dramatically increase and peaked at 218 K. This is shown in Figure 2. Since 1,6-dichlorohexane desorbs at 211 K, which is 18 K lower than the desorption temeprature of biphenyl, the underlayer intruded through the biphenyl overlayer, changing the biphenyl morphology.

The observed enhanced biphenyl fluorescence at 218 K was plotted in Figure 3 as a function of coverage of 1,6-dichlorohexane, $\Theta_{1,6\text{-dichlorohexane}}$. Although the coverage of biphenyl was kept constant as possible at 106 ± 12 M, to account for the slight run-to-run variation in coverage, these intensities were normalized against the biphenyl intensities at λ_{max} = 318 nm at the start of the TPD. The constantsy of the coverage can be seen from the blue plot in which the absolute initial itensities in photon counts during 300 ms at λ_{max} = 318 nm for each of the corresponding bilayer intensities at λ_{max} = 342 nm are shown.

Shown in Figure 4 are the transmittances of the of the excitaion light at 250 nm for biphenyl only and biphenyl in the bilayer with 1,6-dichlorohexane during the TPD. The output trace from the residual gas analyzer is also shown for reference. The disorder-to-order transition can be clearly seen at 160 K, where the transmittance increases due to the fluorescence quenching that occurs because of the opening of the energy transfer pathway. The transmittance shows a dramatic decrease in transmittance precisely when the 1,6-dichlorohexane passes through the biphenyl adlayer on its way to desorption. This can be attributed to a small amount of light scattering as the 1,6-dichlorohexane desorbed from the surface of the Al_2O_3. In addition when ordering occurs, reflection from the surface affects the transmittance and was monitored by noting the intensity of the reflected 365 nm Hg line. However, much of the decrease in transmittance can be attributed to the increase in the absorption of the excitation light by biphenyl. This absorption is proportional to the fluorescence intensity (Cf. red plot in Figure 3, right axis). If the assumption is made that the pathways to excitation and radiative relaxation remain fairly constant with and without the 1,6-dichlorohexane, it is reasonable to conclude that the cause of the enhance fluorescence is the quantity of molecules that can undergo self-excitation and radiative relaxation. This would be analogous to the reason for the decrease in fluorescence intensity upon disorder-to-order transition that is caused by the opening of the non-radiative pathway to relaxation due to the formation of more ordered array of molecules, viz, polycrystalline.

As seen in Figure 4, at the onset of the TPD, the transmittance of the bilayer is higher than that for the biphenyl alone. As seen with the blue graph in Figure 3, the initial fluorescence intensity subsequent to deposition remained relatively constant, *independent* of the presence of the underlayer. However, since the transmittance is higher in the bilayer than with neat biphenyl, and yet with a concommitantly similar fluorescence intensity with and without the underlayer, the biphenyl's quantum yield must be almost twice in the bilayer than by itself. This could be attributed to spacially more isolated biphenyl, particularly at the interface between biphenyl and the underlayer since the 1,6-dichlorohexane had been annealed prior to the deposition of biphenyl. Therefore, the underlayer can be assumed to be already quite ordered.

After the disorder-to-order transition, but prior to the desorption of the underlayer, the transmittances of both the biphenyl alone and in the bilayer are approximately the same. (cf Figure 4). Close examination of this interval in the TPD in the left insets of Figures 1 and 2, indicates that the fluorescence intensity is higher for the bilayer. An explanation of this might be that biphenyl molecules in the bilayer are separated by the ordered structure of 1,6-dichlorohexane in the annealed underlayer. Separated molecules allow for self-excitation and relaxation and a higher fluorescence intensity would be expected.

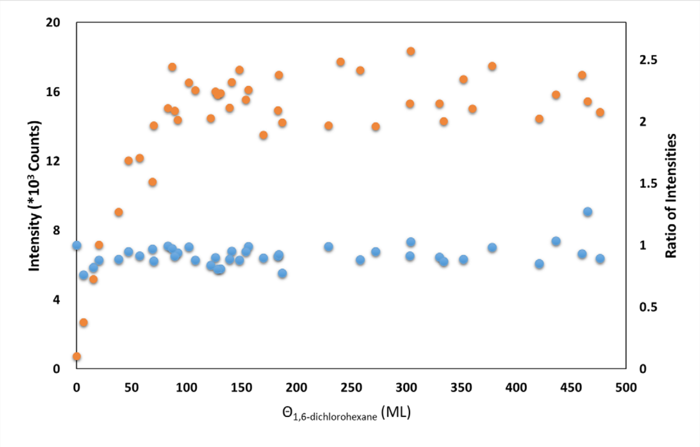

Figure 3. A plot of the intensity of enhanced biphenyl fluorescence (red) and the initial fluorescence intensity (blue) as a function of the coverage of $\Theta_{1,6\text{-dichlorohexane}}$. The coverage of biphenyl, $\Theta_{biphenyl}$, was kept constant at 106 ± 12 ML Red circles: peak of the normalized enhanced fluorescence at λ_{max} = 342 nm at 218 ± 3K during the TPD, right axis. Blue circles: initial intensities of biphenyl at λ_{max} = 318 nm immediately after deposition, left axis.

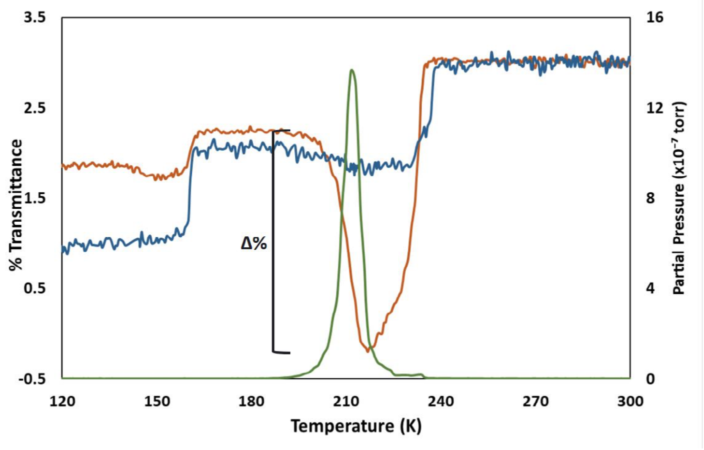

Figure 4. % transmittances during the TPD for biphenyl only with $\Theta_{biphenyl}$ ~114 ML (blue) and for the bilayer with $\Theta_{biphenyl}$ ~119 ML and $\Theta_{1,6\text{-dichlorohexane}}$ ~89 ML (red) (left axis). Superimposed is the output from the residual gas analyzer for 1,6-dichlorohexane with $\Theta_{1,6\text{-dichlorohexane}}$ ~119 ML. (right axis). The increase in transmittance occurs for biphenyl only and in the bilayer due to the disorder-to-order transition at 160 K. The decrease in transmittance for the bilayer is due to the passage of 1,6-dichlorohexane through the biphenyl adlayer before desoportion. The Δ% is plotted as a function of $\Theta_{1,6\text{-dichlorohexane}}$ in Figure 5.

When there is sufficent number of 1,6-dichlorohexane molecules to cause the maximum enhancement of biphenyl flourescence, the increase levels off. This level off point occurs when the stochiometric ratio is approximately 1 molecule of 1,6-dichlorhexane per molecule of biphenyl. Both the intensity of the enhanced fluorescence as shown in Figure 3 and the change in transmittance as shown in Figure 5 support this stoichiometric ratio. Although there is need of further investigation, this ratio is significant in that the size of the perturbing molecule, 1,6-dichlorohexane in this case, matches that of the biphenyl fluorophore. (Vide infra).

Two preliminary evidences give support to the unusually strong interaction of 1,6-dichlorohexane and biphenyl. The first is shown in Figure 6 in which the peak desorption temperatures are recorded for biphenyl and 1,6-dichlorohexane. Here again, $\Theta_{biphenyl}$ was kept constant at 106 ± 12 ML. Although the biphenyl desorbed at its normal desorption temperature of 229 ± 3 K, 1,6-dichlorohexane's desorption temperature increased monotonically with coverage. This is a clear indication that 1,6-dichlorohexane interacts with biphenyl.

The second evidence is that, although not shown here, LIF of biphenyl was measured for pure and in the bilayer. Upon deposition, the lifetime of biphenyl itself was about 37 ns and then increased to 67 ns at the disorder-to-order transition. This is because the ordered biphenyl is separated further apart in the ordered state. When 1,6-dichlorohexane passed through the biphenyl, the lifetime shortened from 67 ns to about 50 ns. The shorter lifetime is a good indicator of interaction of the fluorophore with the 1,6-dichlorohexane which opens another pathway for relaxation.

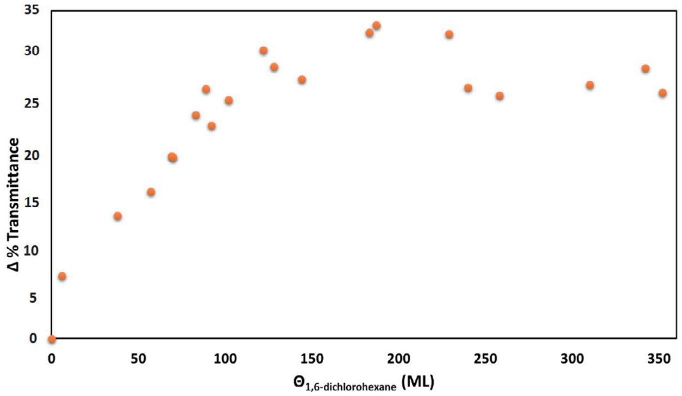

Figure 5. The change in the transmittance (Δ% shown in Figure 4) is plotted as a function of $\Theta_{1,6\text{-dichlorohexane}}$ .The coverage of biphenyl, $\Theta_{biphenyl}$, was kept constant at 106 ± 12 ML As in Figure 3, the leveling of the slope occurs at slightly more than 100 ML.

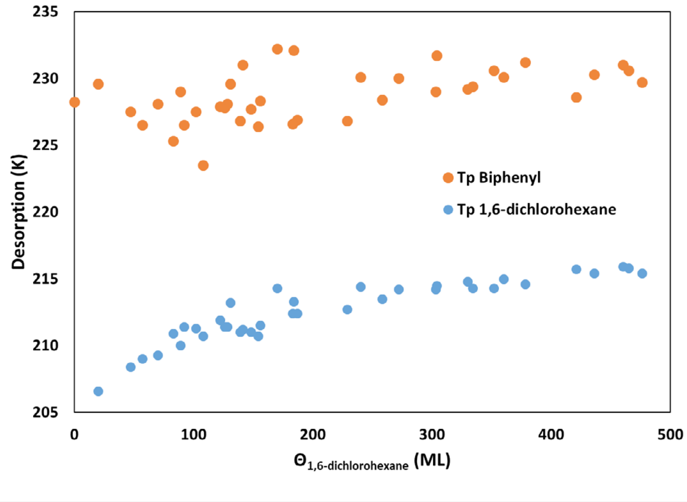

Figure 6. For the bilayer, T_p, the peak desorption temperatures of 1,6-dichlorohexane (blue) and of biphenyl (red). Note the gradual increase in the T_p for 1,6-dichlorohexane while the T_p of biphenyl remains relatively constant. The coverage of biphenyl, $\Theta_{biphenyl}$, was kept constant at 106 ± 12 ML

In order to understand more fully the state of biphenyl after 1,6-dichlorohexane has desorbed, the following experiment was performed. The bilayer was formed and the temperature was ramped to 218 K for 5 seconds. Since the T_p for 1,6-dichlorohexane is 211 K, most had desorbed at this point, but had prepared the biphenyl in the state which was intensely emissive. The sample was then allowed to cool to the original deposition temperature of 120 K. This was followed by a normal TPD. The result is shown in Figure 7. The right inset shows the annealing run at 218 K in which most of the 1,6-dichlorohexane was desorbed. Note that the final intensity is about 9,000 photon counts. When the sample was allowed to cool to 120 K and the TPD experiment was done, the intensity began at about 7000 counts and then increased to >9,000 counts at about 180 K. The observation that the fluorescence intensity returned to approximately the intensity as when the temperature ramp was stopped, even though the 1,6-dichlorohexane had desorbed at this point, means that the biphenyl was irreversibly left in a state of high emissivity and that this state did *not* require the presence of 1,6-dichlorohexane. Finally, the strength of the interaction between the biphenyl and 1,6-dichlorohexane can be estimated by the T_p of 224 K for the few remaining underlayer molecules that desorbed *with* the biphenyl during the TPD. (Compare this T_p with the blue plot in Figure 6)

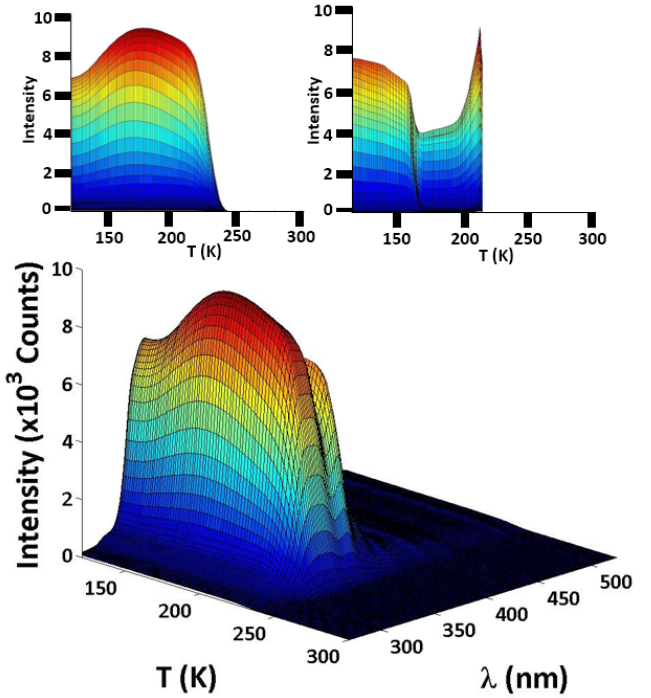

Figure 7. Spectra of biphenyl that had been prepared in the state after the desorption of 1,6-dichlorohexane. The right inset shows the intensity versus temperature in which the sample was annealed at 218 K for 5 s. After cooling to the original deposition temperature of 120 K, the spectra is shown as a function of temperature in the top left inset. The main figure is the diagonal view of the left inset.

What can be concluded from the study thus far are, first, that the 1,6-dichlorohexane interacts relatively strongly with biphenyl as it percolates through the biphenyl adlayer. Since no other molecular underlayer enhanced the fluorescence of biphenyl to the extent that 1,6-dichlorohexane does, this uniqeness must be attributed to the molecule's structure relative to biphenyl. It is with this in mind that the conformer to the carbon backbone is postulated to be more U shaped (Cf. Scheme 1) which would allow for the two chlorines to interact with the two aromatic electronic clouds at the same time. This interaction has been attributed by others to the halogen bond or Cl-π interaction.[13-14] This is due to the electrostatic interaction between the positive σ-hole on the chlorine and the negative electronic charge density on the aromatic ring.[13-14] Such interaction which understandably is not as strong as a hydrogen bond, but stronger than dispersion forces alone, has been reported to cause the Cl to approach the π-cloud at distances of about 4.5 Å.[13-14]

The second conclusion is that when the 1,6-dichlorohexane is percolating and moving through the biphenyl adlayer, this Cl-π interaction causes the overlayer of biphenyl in its ordered state to fracture in its wake, thereby increasing the density of defect sites from which radiative relaxation can occur. In addition, this interaction could also cause the isolation of biphenyl molecules beyond the Förster energy transfer distances (recall that for neat biphenyl, energy transfer caused the decreased intensity subsequent to the disorder-to-order transition). If this were the case, enhanced fluorescence intensity is postulated to occur by self-excitation-relaxation pathway.

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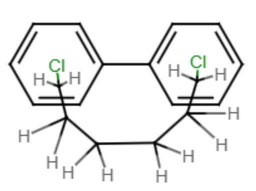

Scheme 1. Postulated structure of the biomolecular complex of biphenyl and 1,6-dichlorohexane via the Cl-π interaction.

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Results of Supplemental Experiments

Is it the chlorines or the hexyl hydrocarbon moiety in 1,6-dichlorohexane that is a necessary component in the enhanced biphenyl fluorescence? Two experiments were done in an attempt to answer this question.

biphenyl/n-hexane

How does hexane moiety alone affect the biphenyl fluorescence upon percolation and desorption? Shown in Figure 8 is the wavelength-resolved TPD of biphenyl with *n*-hexane as the underlayer. Low coverage *n*-hexane on Al_2O_3 has a T_p of 146 K and a E_a of 36 kJ/mol.[1] (T_p and E_a of this and all compounds in this study are summarized in Table 1). In contrast to Figure 1, the 318 nm fluorescence that is normally expected with the twisted conformer that dominate the fluorescence has almost disappeared, The intensity is in the peaks at λ_{max} of 370 and 332 nm that has been assigned to the excimer and trap emissions, respectively.[1,2,14-15] Then at 156 K, subsequent to the desorption of the *n*-hexane, these two peaks at 370 and 332 intensified to twice the initial intensities. (Cf. left inset in Figure 8) The percolation of *n*-hexane caused biphenyl in the twisted conformer to become planar. Hence as can be seen from the right inset, the emitting species are the excimer at 370 nm and the monomer at 332 nm. Then the disorder-to-order transition caused the excimeric species to become monomeric and ordered. Consequently, the fluorescence wavelength shifted to 332 nm and this planar conformer of biphenyl was the only emitter present this far beyond the disorder-to-order transition during the TPD. Since hexane creates a very different underlayer morphology, the hydrocarbon backbone may not be responsible for the increased intensity.

Possible observation of even-odd effect in the interaction of $\alpha-\omega$ *dichloroalkanes with biphenyl.*

In this study, other 1,ω−dichloroakanes underlayer com-

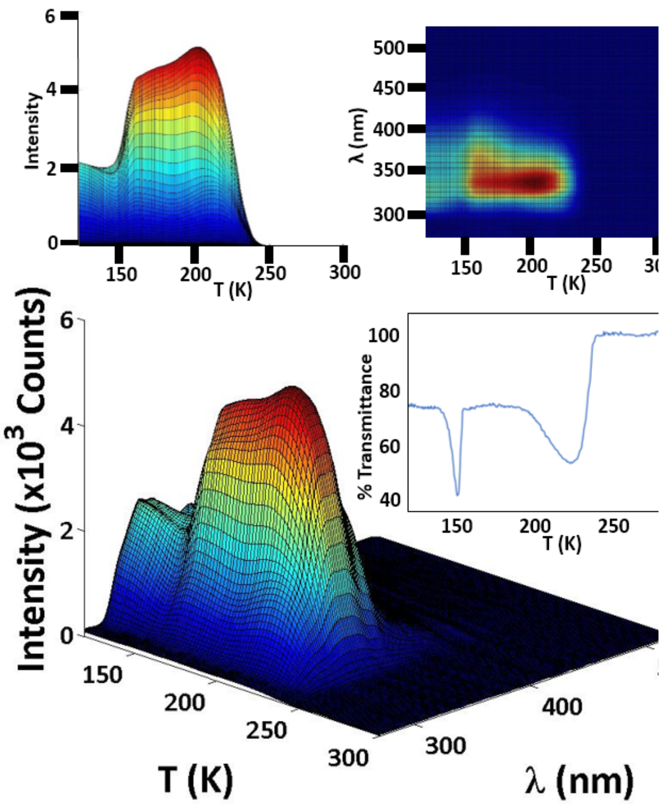


Figure 8: Wavelength-resolved TPD of biphenyl with $\Theta_{n\text{-hexane}}$ = 209 ML and $\Theta_{biphenyl}$ 105 ML. The λ_{max} at 318 nm peak that is usually observed at deposition has minimal intensity. At 156 ±1.4 K, the fluorescence intensities at λ_{max} 332 nm and 370 nm are enhanced. Left and right insets: side view and top views, respectively. The right middle inset is % transmittance.

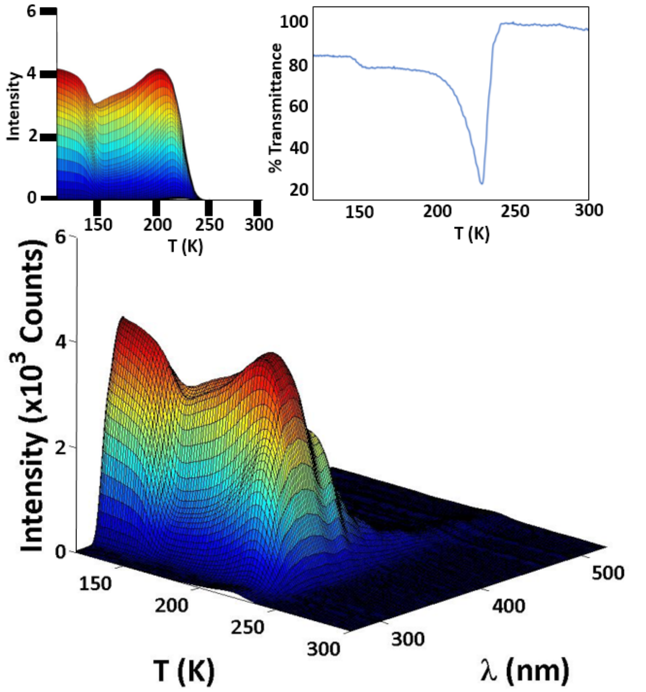


Figure 9: Wavelength-resolved TPD of 1,8-dichlorooctane/biphenyl bilayer with $\Theta_{1,8\text{-dichlorooctane}}$ = 106 ML and $\Theta_{biphenyl}$ 124 ML. The underlayer was annealed at 200 K for 30 s. The λ_{max} at 318 nm peak that is usually observed at deposition is clearly visible. At 160 K, the fluorescence red-shifts slight to λ_{max} 325 nm . Left and right insets: side view and transmittance vs. temperature, respectively.

pounds were studied. One noteworthy observation in the homologous series of 1,ω –dichloroalkanes is how the 1,2-dichloroethane, 1,4-dichlorobutane, 1,6-dichlorohexane and 1,8-dichlorooctane exhbit progressive increase in the fluorescence in biphenyl. (See Figures 9-14). What is particularly interesting is that the even-odd effect is typically associated with molecular orientation on surfac-

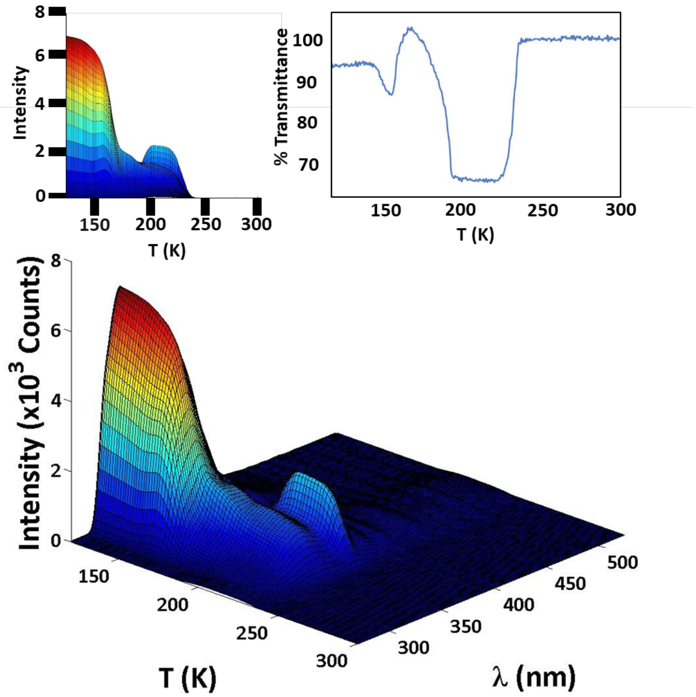


Figure 10. 1,5-dichloropentane/biphenyl bilayer. $\Theta_{1,5\text{-dichloropentane}}$ = 155 M and $\Theta_{biphenyl}$ = 103 ML. The underlayer was annealed at 170 K for 30 seconds prior to the deposition of biphenyl. Insets: left is the intensity versus temperature, side view. On the right is the transmittance of the 250 nm excitation light.

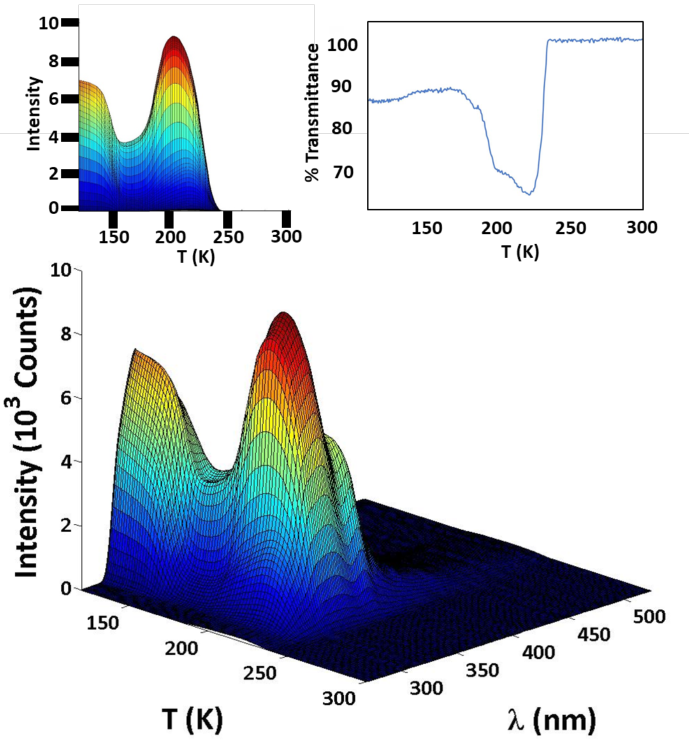


Figure 11. 1,4-dichlorobutane/biphenyl bilayer with $\Theta_{1,4\text{-dichlorobutane}}$ = 220 ML and $\Theta_{biphenyl}$ = 130 ML. The underlayer was annealed at 160 K for 30 seconds prior to the deposition of biphenyl. Insets: left is the intensity versus temperature, side view. On the right is the transmittance of the 250 nm excitation light.

es, but here, the even-odd effect appear to apply directly to organic self-assembled monolayers.[17-18] The most effective underlayer in this list was 1,4-dichlorobutane (See Figure 11), where Cl-π interaction is possible. (Cf. Scheme 2).

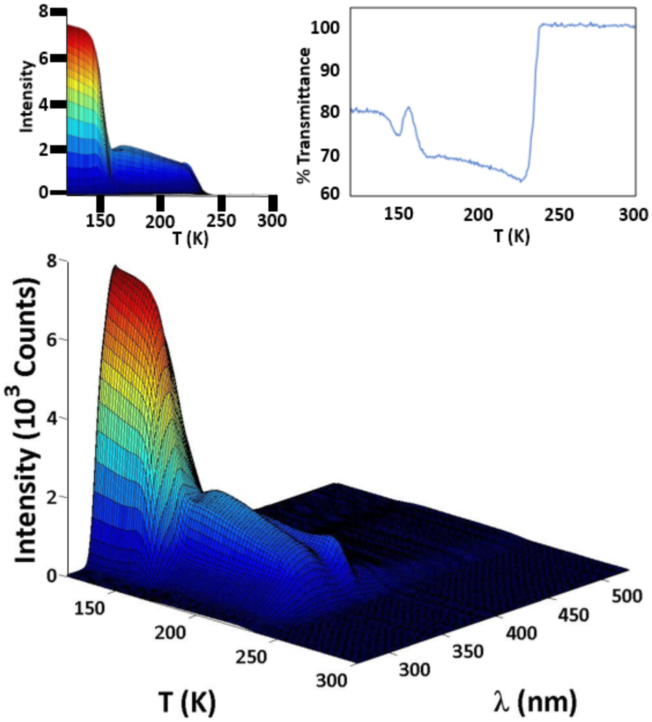


Figure 12. 1,3-dichloropropane/biphenyl bilayer. $\Theta_{1,3\text{-dichloropropane}}$ = 136 ML Θ_{biphenyl} = 120 ML The underlayer was annealed at 130 K for 30 seconds prior to the deposition of biphenyl. Insets: left is the side view of intensity versus temperature, side view. On the right is the transmittance of the 250 nm excitation light.

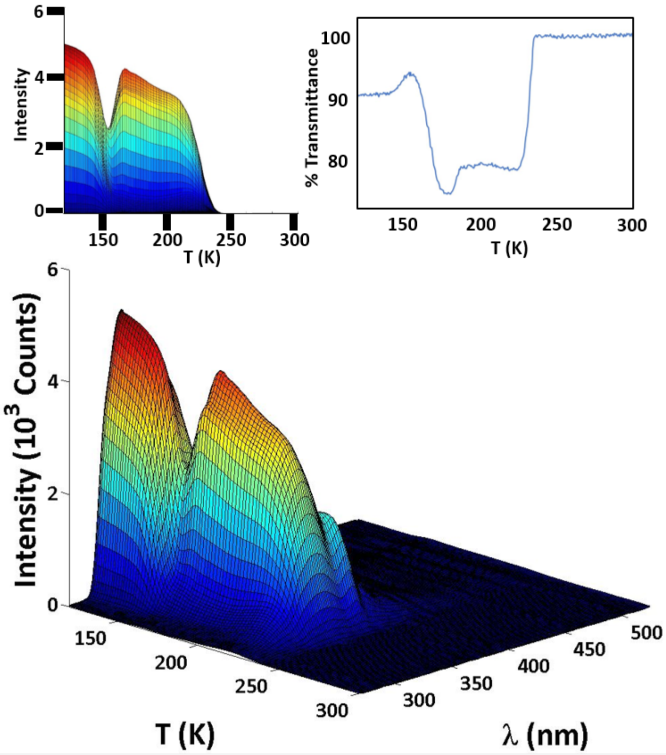


Figure 13. 1,2-dichloroethane/biphenyl bilayer with $\Theta_{1,2\text{-dichloroethane}}$ = 115 MLand Θ_{biphenyl} = 93 ML. The underlayer was annealed at 130 K for 15 s prior to the deposition of biphenyl. Insets: left is the intensity versus temperature, side view. On the right is the transmittance of the 250 nm excitation light.

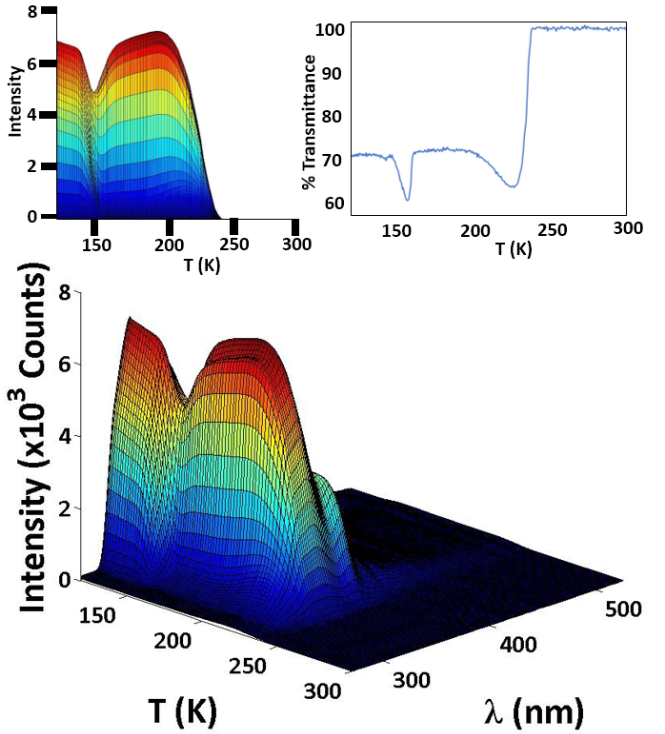
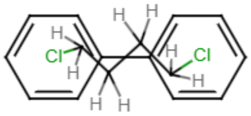


Figure 14. dichloromethane/biphenyl bilayer. Coverages were: $\Theta_{\text{dichloromethane}}$ = 108 ML and Θ_{biphenyl} = 107 ML. Dichloromethane was not annealed. Insets: left is the intensity versus temperature, side view. On the right is the transmittance of the 250 nm excitation light.

Table 1. Activation energies in kJ/mol for all of the compounds in this study as calculated from T_p's[8-10].

Absorbate	T_p(K)	E_a(kJ/mol)	E_a Percent Error
dichloromethane	143 ± 3	37 ± 1	3%
1,2-dichloroethane	161 ± 2	41.3 ± 0.3	0.7%
1,3-dichloropropane	163 ± 3	42 ± 1	2%
1,4-dichlorobutane	184 ± 4	47 ± 1	2%
1,5-dichloropentane	188 ± 2	48 ± 0.5	1.0%
1,6-dichlorohexane	211 ± 3	55 ± 0.6	1.1%
1,8-dichlorooctane	227 ± 1	58.9 ± 0.2	0.3%
hexane	147 ± 2	37.7 ± 0.4	1%
biphenyl	229 ± 1	59.5 ± 0.2	0.3%



Scheme 2. Postulated structure of the biomolecular complex of biphenyl and 1,4-dichlorobutane via the Cl-π interaction.