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EVIDENCE FOR FORMATION OF THE BIPHENYL-NAPHTHALENE EXCIPLEX ON Al_2O_3 VIA DESORPTION-INDUCED MOLECULAR INTERMIXING USING A SACRIFICAL CYCLOHEXANE SPACER

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Abstract

Observation of the naphthalene–biphenyl excited state dimer, exciplex, has remained elusive despite numerous experimental attempts. A likely limitation is the nonplanar geometry of biphenyl, which reduces the close intermolecular contact and orbital overlap required for exciplex formation. Previous studies relying solely on thermally induced intermixing of separately deposited naphthalene and biphenyl adlayers during temperature-programmed desorption (TPD) failed to produce convincing spectroscopic evidence for the exciplex. In the present work, a sacrificial cyclohexane underlayer, possessing a lower desorption temperature than either aromatic fluorophore, was employed to promote desorption-induced molecular intermixing. As the cyclohexane desorbs, transient dispersion interactions with the aromatic overlayers facilitate molecular redistribution and increase the probability of naphthalene–biphenyl encounters. Under these conditions, a previously unobserved broad, featureless emission centered at approximately 430 nm was detected. The spectral characteristics of this emission are consistent with those expected for a naphthalene–biphenyl exciplex, suggesting that desorption-induced molecular intermixing provides an effective strategy for promoting exciplex formation in vapor-deposited molecular films.

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Introduction

Numerous attempts have been made over the years to observe the naphthalene–biphenyl exciplex.[1-6] A major obstacle to its formation is the molecular geometry of biphenyl when vapor-deposited onto an Al_2O_3 surface.[7] Whereas the gas-phase molecule adopts a twisted equilibrium geometry due to steric repulsion between the ortho (α) hydrogen atoms, a planar conformation can be stabilized on surfaces due to increased π-electron delocalization.[7] On Al_2O_3 surface, however, biphenyl remains sufficiently twisted to reduce orbital overlap with adjacent naphthalene molecules, thereby decreasing the probability of exciplex formation.[1-6]

Previous efforts to generate this exciplex involved the sequential vapor deposition of the two molecules as separate adlayers.[1-6] During temperature-programmed desorption (TPD), thermal motion was expected to promote intermolecular contact prior to desorption. In initial experiments, biphenyl was deposited as the overlayer and naphthalene as the underlayer because the desorption temperature of biphenyl is approximately 15 K higher than that of naphthalene.[1-6] An intense fluorescence band centered near 338 nm was observed in the temperature region where trap emission from both species occurs. While initially attributed to exciplex formation,[1-6] this assignment remained tentative since the spectrum lacked the characteristic properties of an exciplex, showing no substantial red-shift or broadness despite the absence of vibrational fine structure.[1-6]

More recently, studies of alkane underlayers revealed a previously unrecognized mechanism influencing molecular organization during TPD.[8-10] For alkanes with desorption temperatures lower than that of the aromatic overlayer, desorption creates an interfacial void beneath the overlayer.[8-10] The aromatic film remains temporarily suspended above the substrate, maintaining structural stability until sufficient thermal energy overcomes the activation barrier for collapse.[8-10] Within this suspended-overlayer model, the extent of structural reorganization during collapse determines the degree of film disorder. For naphthalene—where excimer formation is favored in the disordered phase relative to the ordered morphology—collapse of the suspended overlayer significantly enhances excimer fluorescence while simultaneously increasing structural defects and trap emission.[8-10]

These observations suggested a new strategy for promoting naphthalene–biphenyl exciplex formation. Rather than relying solely on thermal diffusion near desorption temperatures, a sacrificial alkane underlayer could drive desorption-induced molecular intermixing at an earlier stage of the TPD experiment. As the alkane desorbs, transient molecular redistribution and interfacial reorganization should increase the frequency of heteromolecular encounters, enhancing the probability of exciplex formation before either aromatic species desorbs.

Cyclohexane was selected as the candidate underlayer because its six-carbon cyclic framework provides a molecular size and contact area comparable to the aromatic rings of naphthalene and biphenyl. Consequently, cyclohexane was expected to interact efficiently with the overlayer via dispersion forces during desorption, facilitating the close intermolecular contact required for exciplex formation.

Experimental

Materials and Substrate Preparation

High-purity biphenyl, naphthalene and cyclohexane (>99%) were obtained from commercial suppliers (Sigma-Aldrich, St. Louis, MO, USA, and TCI America, Portland, OR, USA) and used without further purification. Each compound was loaded into a stainless-steel reservoir connected to a precision leak valve to permit controlled vapor deposition under ultra-high vacuum (UHV) conditions.

Experiments were performed in a UHV chamber with a hydrogen base pressure of approximately 1×10^{-9} Torr. The substrate was a single-crystal $Al_2O_3(0001)$ wafer (Crystal Systems, Inc., Salem, MA, USA), suspended from the cold finger of a liquid-ni-

trogen cryostat. The crystal was mounted between two copper support posts using a sapphire spacer to provide electrical isolation while maintaining good thermal contact with the cryostat. Resistive heating was achieved by passing current through a thin tantalum foil in thermal contact with the back face of the crystal. The substrate temperature was monitored with a type-K (chromel–alumel) thermocouple (Omega Engineering, Norwalk, CT, USA) attached directly to the rear surface of the crystal.

Temperature-Programmed Desorption

Temperature-programmed desorption (TPD) experiments were controlled using a custom LabVIEW program (National Instruments, Austin, TX, USA). A proportional-integral-derivative (PID) feedback algorithm maintained a linear heating rate of 1.98 ± 0.01 K s^{-1} (approximately 2 K s^{-1}). Following each experiment, the substrate was flashed to 300 K to remove residual adsorbates and restore a reproducible starting surface. Additional heating to higher temperatures produced no detectable desorption, confirming complete surface regeneration.

The adsorbed fluorophores were excited with the 250 nm line from a high-pressure mercury lamp coupled to a 0.25 m monochromator. Fluorescence emitted from the sample was collected using a quartz lens and light-pipe assembly and transmitted through a vacuum feedthrough to an ultraviolet-sensitive Ocean Optics SR2 UV–Vis spectrometer (Ocean Optics, Orlando, FL, USA). During each TPD experiment, complete fluorescence spectra were acquired every 300 ms. The resulting wavelength-, temperature-, and intensity-resolved data sets were analyzed using custom MATLAB software (MathWorks, Natick, MA, USA) to generate the fluorescence contour plots and wavelength-resolved TPD profiles presented in this work.

Coverage Calibration

The LabVIEW acquisition system simultaneously interfaced with a residual gas analyzer (RGA) to monitor mass-spectrometric signals during both deposition and desorption. Surface coverages, Θ, expressed in monolayers (ML), were determined by calibrating the integrated mass spectrometer signals against independent optical interference measurements. This calibration yielded deposition rates with an estimated uncertainty of ±30%, following procedures described previously.[11]

Results

Following the methodology established in our recent investigations, the fluorescence spectra of multilayer naphthalene and multilayer biphenyl were first characterized to serve as reference systems.[1-10] To track the dynamics of the film during heating, we utilized our finding that hydrocarbon underlayers with low desorption temperatures generate a transient interfacial void during TPD.[8-10] As the hydrocarbon desorbs and percolates through the aromatic overlayer, transient solvation of the fluorophore yields characteristic monomer fluorescence.[8-10] The onset of this monomer emission provides a convenient spectroscopic marker for the desorption temperature of the cyclohexane underlayer.

The physical dimensions and consequences of this transient void beneath the overlayer were monitored through two complementary photophysical indicators:

- *Excimer Fluorescence*: The volume of the evacuated interfacial space was inferred qualitatively from the magnitude of the excimer fluorescence observed during film collapse.[8-10] Because larger voids permit greater molecular freedom prior to collapse, they yield larger enhancements in excimer fluorescence.[8-10]
- *Trap Fluorescence*: Serving as an independent measure of structural disorder, trap emission originates from defect sites introduced during the disorder-to-order phase transition of the multilayer film.[8-10] An increase in trap intensity indicates that the collapse and subsequent reorganization of the suspended overlayer generate additional lattice defects and highly disordered domains within the crystalline matrix.

Our hope was that by using cyclohexane as a sacrificial underlayer, its strong van der Waals interactions and subsequent desorption would induced the molecular mixing of the naphthalene and biphenyl layers. This structural disruption might facilitate the close intermolecular contact necessary for bipheny and naphthalene to yield a new, distinct emission.

Multilayer Naphthalene and Multilayer Biphenyl

Figures 1 and 2 present the wavelength-resolved TPD spectra of multilayer naphthalene and multilayer biphenyl, respectively, establishing the spectroscopic baselines for subsequent bilayer and trilayer experiments.

Vapor-deposited naphthalene forms an amorphous adlayer on Al_2O_3. Optical excitation produces the characteristic broad, featureless excimer emission centered at λ_{max} = 398 nm. During TPD, the film undergoes a disorder-to-order transition beginning near 190 K. Monomer fluorescence reaches a maximum at approximately 205 K, immediately preceding desorption at about 210 K. (See Figure 1)

Figure 2 shows the corresponding wavelength-resolved TPD spectrum for multilayer biphenyl. In the gas phase, biphenyl adopts a twisted geometry with a dihedral angle of approximately 45°.[7] The amorphous vapor-deposited film exhibits fluorescence centered near 320 nm. As the temperature increases, fluorescence decreases gradually because of thermal quenching until the onset of the disorder-to-order transition near 155 K, which is completed by approximately 165 K. During this transition the fluorescence intensity decreases dramatically, reaching approximately 10% of its initial value, reflecting the formation of a highly ordered crystalline phase. Simultaneously, the fluorescence maximum shifts from approximately 320 to 340 nm, consistent with increased intermolecular interactions and a more planar molecular conformation in the ordered film.[1]

Cyclohexane–Fluorophore Bilayers

To establish that cyclohexane effectively promotes structural reorganization in both fluorophores, bilayers consisting of cyclohexane underlayers with either naphthalene or biphenyl overlayers were investigated. The wavelength-resolved TPD spectra are shown in Figures 3 and 4.

For the cyclohexane/naphthalene bilayer, cyclohexane desorbs at approximately 147 K. At this temperature, weak trap emission first becomes evident, while the excimer intensity increases substantially, reaching a maximum near 157 K or about

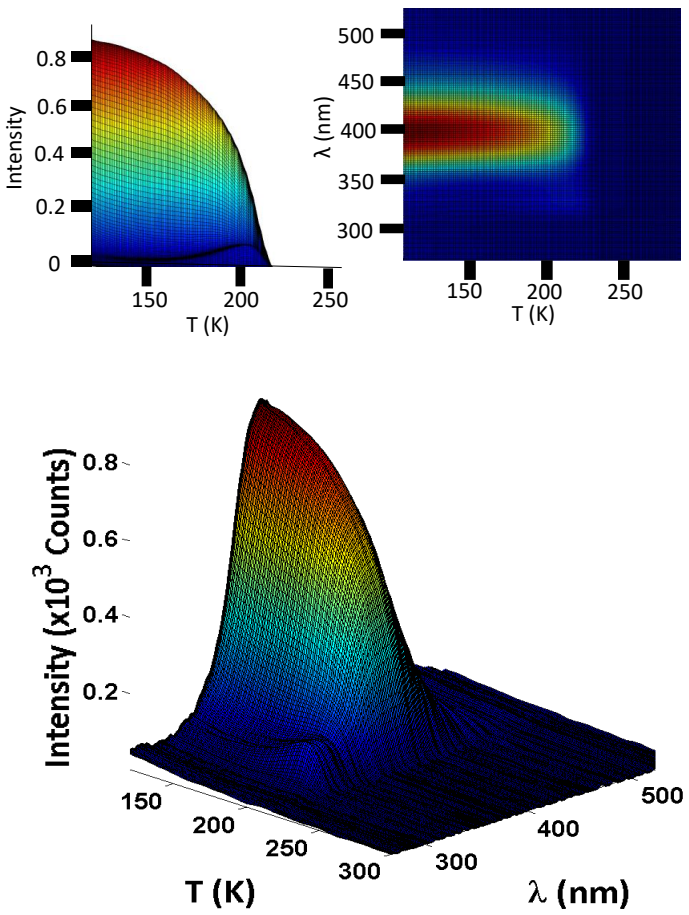

Figure 1. Wavelength-resolved TPD of naphthalene neat with coverage of 87 ML. The excimer has a λ_{max} = 398 nm. The disorder-to-order transition occurs at 205 K during the TPD, but the trap emission from the ordered state is barely visible. Left inset: Fluorescence intensity vs. T during the TPD. Right inset: top view.

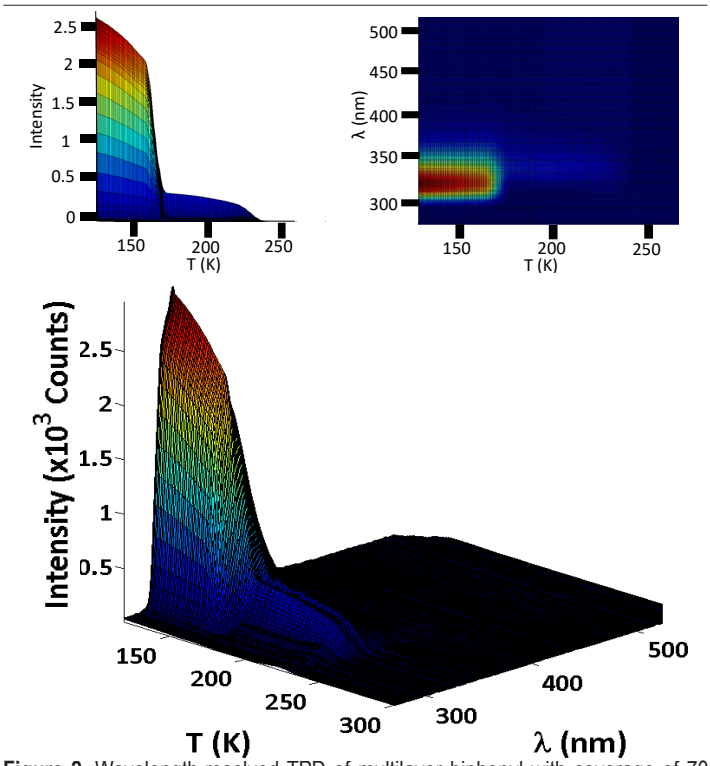

Figure 2. Wavelength-resolved TPD of multilayer biphenyl with coverage of 70 ML. The amorphous biphenyl fluorescence has λ_{max} = 320 nm. The disorder-to-order transition occurs at 160 K and red-shifts to 340 nm with a concommitant decrease in the intensity to about 10% of its initial value. Left inset: Intensity vs. T during the TPD. Right inset: top view.

10 K additional thermal energy is required to overcome the barrier for the collapse of the suspended layer. Trap emission reaches its maximum at approximately 200 K, followed by naphthalene desorption near 211 K. These observations are consistent with the suspended-overlayer model developed previously.

For the cyclohexane/biphenyl bilayer, cyclohexane desorbs at approximately 149 K. Biphenyl is initially deposited in the twisted conformation, as evidenced by its 320 nm emission. Structural reorganization begins at approximately 150 K, nearly 10 K earlier than observed for multilayer biphenyl, but coincident with cyclohexane desorption. The fluorescence subsequently red-shifts toward 335 nm, indicating increasing planarity of the biphenyl molecules. Maximum fluorescence intensity is observed near 165 K, whereas biphenyl desorption occurs at approximately 225 K. The 15 K interval between cyclohexane desorption and maximum fluorescence is attributed to the temperature required for collapse and structural reorganization of the suspended biphenyl overlayer.

Naphthalene–Biphenyl Bilayers

To determine whether exciplex formation occurs in the absence of cyclohexane-induced molecular intermixing, bilayers consisting solely of naphthalene and biphenyl were examined. Figures 5 and 6 show the wavelength-resolved TPD spectra for naphthalene/biphenyl and biphenyl/naphthalene bilayers, respectively.

For the naphthalene underlayer with biphenyl overlayer, biphenyl deposits predominantly in a planar conformation, consistent with growth on the planar naphthalene surface. Fluorescence intensity increases until approximately 160 K, corresponding to the biphenyl disorder-to-order transition, and then increases again above 200 K, reaching a maximum near 215 K. Throughout the TPD experiment, naphthalene remains predominantly excimeric, exhibiting only a gradual decrease in fluorescence intensity prior to desorption.

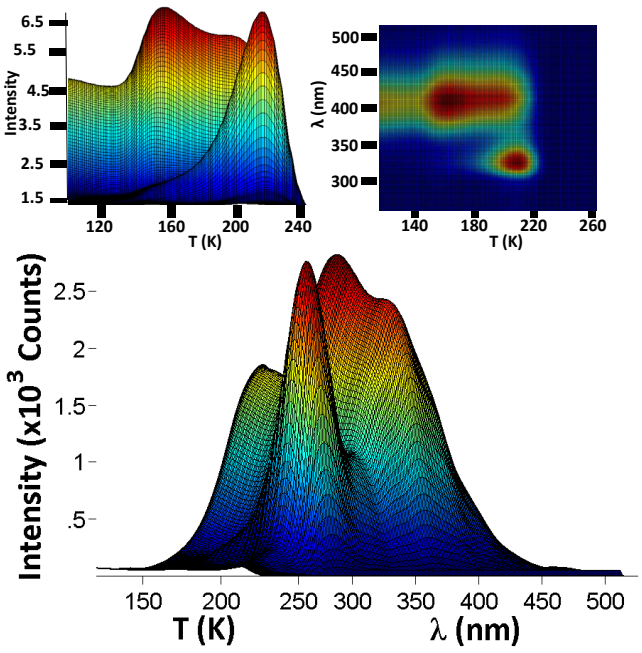

Figure 3. Wavelength-resolved TPD of naphthalene with $\Theta_{naphthalene}$ = 45 ML with an underlayer of cyclohexane with $\Theta_{cyclohexane}$ = 113 ML. Left inset: fluorescence intensity vs T during the TPD. Right inset: top view.

In contrast, biphenyl deposited beneath a naphthalene overlayer retains the twisted conformation characteristic of multilayer biphenyl. At approximately 160 K, biphenyl undergoes its characteristic disorder-to-order transition accompanied by a pronounced decrease in fluorescence intensity and the expected red shift. Naphthalene excimer emission decreases concurrently. Near 222 K, a strong trap emission develops. Previous work attributed this feature to exciplex formation; however, the present results suggest that the emission is more appropriately assigned to defect-site fluorescence generated during structural reorganization rather than to exciplex emission.

Cyclohexane–Naphthalene–Biphenyl Trilayers

Figures 7 and 8 show wavelength-resolved TPD spectra for trilayers consisting of cyclohexane underlayers with naphthalene/biphenyl and biphenyl/naphthalene overlayers, respectively.

In both trilayer systems, the intense emission observed near 340 nm at approximately 210 K is assigned to the combined trap fluorescence of naphthalene and biphenyl. Because both fluorophores contribute to the defect-site emission within this spectral region, the resulting intensity is substantially greater than that observed for either fluorophore individually.

More significantly, careful examination of the long-wavelength emission shown in Figure 8 reveals a previously unrecognized fluorescence band centered near 430 nm in addition to the characteristic naphthalene excimer centered at 398 nm. Spectral deconvolution shown in Figure S3 of the slice at 200-210K shown by the red arrow indicates that this broad emission envelope consists of two components, with the 430 nm band contributing approximately 35% of the total integrated intensity. The 430 nm feature exhibits a full-width-at-half-maximum (FWHM) of approximately 70 nm, which is nearly identical to that of the 398 nm excimer band. In comparison, the peak due to traps at 340 nm has a FWHM of 25 nm. Unlike the previously assigned 340 nm feature, this emission at 430 nm is both substantially red-shifted and broad, possessing the spectroscopic characteristics expected for exciplex fluorescence.

The supplementary trilayer experiments (Figures S1 and S2) provide additional support for this interpretation. In particular, the biphenyl/cyclohexane/naphthalene trilayer likewise exhibits a broad, featureless emission near 430 nm. This is in addition to

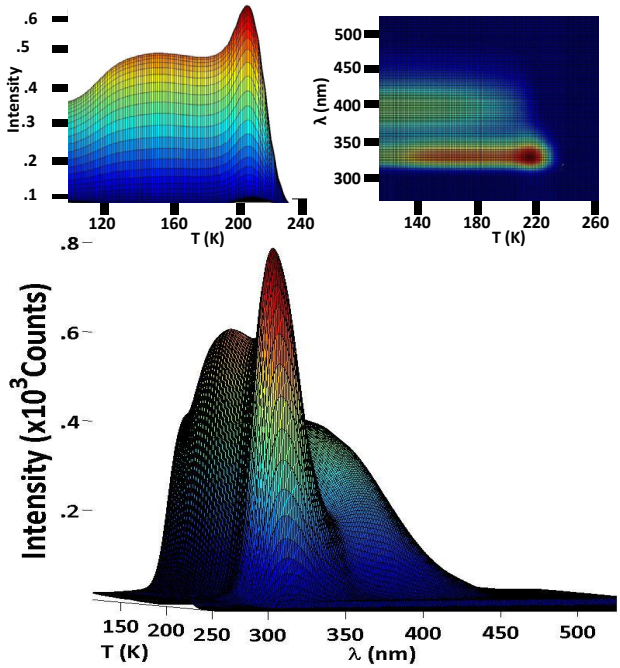

Figure 5. Wavelength-resolved TPD of biphenyl with $\Theta_{biphenyl}$ = 148 ML. with an underlayer of naphthalene $\Theta_{naphthalene}$ = 164ML. Left inset: fluorescence intensity vs T during the TPD. Right inset: top view.

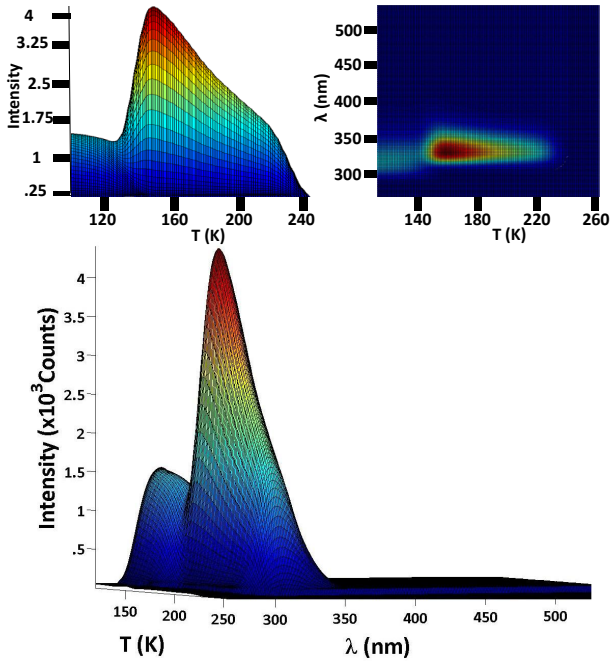

Figure 4. Wavelength-resolved TPD of biphenyl with $\Theta_{biphenyl}$ = 63 ML with an underlayer of cyclohexane with $\Theta_{cyclohexane}$ = 145 ML. Left inset: fluorescence intensity vs T during the TPD. Right inset: top view.

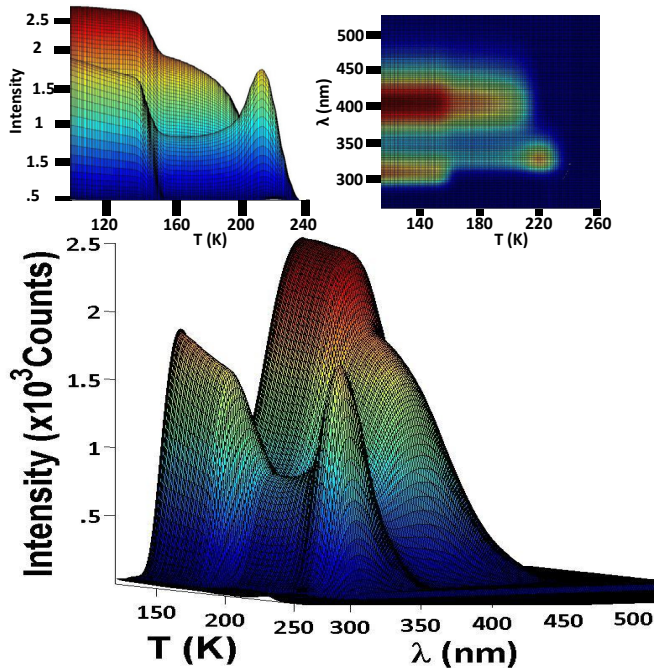

Figure 6. Wavelength-resolved TPD of naphthalene with $\Theta_{naphthalene}$ = 107 ML with an underlayer of biphenyl with $\Theta_{biphenyl}$ = 93 ML. Left inset: fluorescence intensity vs T during the TPD. Right inset: top view.

the naphthalene excimer commonly observed in this region. It is consistent with the formation of the same emissive species in the above mentioned deposition sequence.

Discussion

Several lines of evidence support the assignment of the newly observed 430 nm emission band to the long-sought naphthalene–biphenyl exciplex:

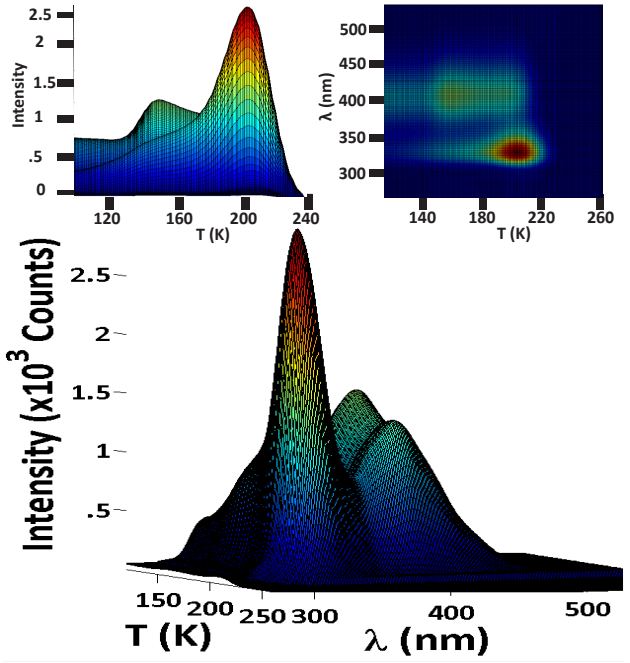

Figure 7. Wavelength-resolved TPD of trilayer consisting of cyclohexane with $\Theta_{cyclohexane}$ = 97 ML, naphthalene with $\Theta_{naphthalene}$ = 39 ML with an overlayer of biphenyl with $\Theta_{biphenyl}$ = 64 ML. . Left inset: fluorescence intensity vs T during the TPD. Right inset: top view.

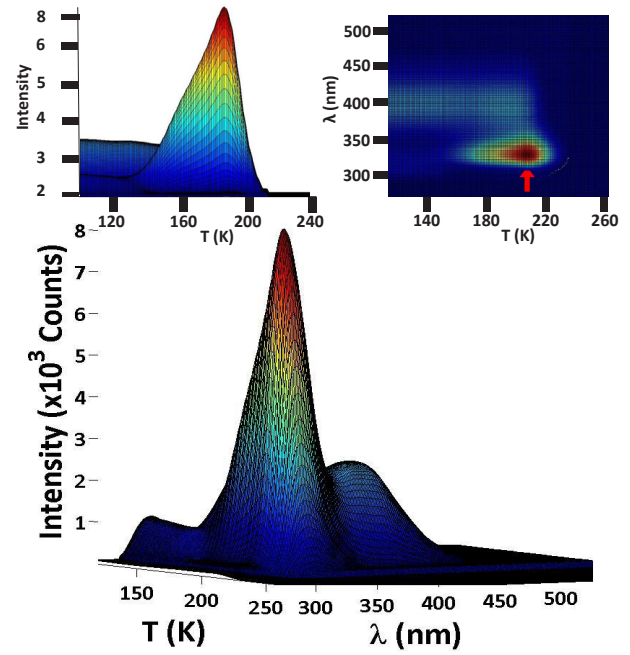

Figure 8. Wavelength-resolved TPD of trilayer consisting of cyclohexane with $\Theta_{cyclohexane}$ = 165 ML, biphenyl with $\Theta_{biphenyl}$ =85 ML. with an overlayer of naphthalene with $\Theta_{naphthalene}$ = 57 ML Left inset: fluorescence intensity vs T during the TPD. Right inset: top view. Red arrow indicates spectral slice taken to do the deconvolution shown in Figure S3.

- *Significant Red-Shift*: The emission is markedly red-shifted relative to the monomer fluorescence of both naphthalene and biphenyl, a benchmark trait of excited state complex, exciplex.[13]
- *Spectral Profile*: The band is broad and featureless, exhibiting a full-width-at-half-maximum (FWHM) of approximately 70 nm. This profile is highly consistent with the known FWHM values of the naphthalene excimer (65 nm)[8,13] and the biphenyl excimer (70 nm).[12] This FWHM similarity is what is expected for an exciplex.
- *Distinct Peak Position*: The emission maximum at 430 nm is reasonably well-resolved from other potential emissive species in the system, namely the naphthalene excimer ($\lambda_{max} \approx 398$ nm)[8,13] and the biphenyl excimer ($\lambda_{max} \approx 370$ nm),[12] confirming the generation of a unique excited-state complex.
- *Thermal Correlation*: The 430 nm band emerges precisely within the TPD temperature range where desorption-induced molecular intermixing is maximized. During this window, the collapse and structural reorganization of the suspended overlayers maximize heteromolecular encounters.
- *Emission Intensity*: The relatively low intensity of the 430 nm emission is entirely consistent with exciplex dynamics. Because homomolecular interactions leading to excimer formation are statistically and thermodynamically favored over heteromolecular interactions, only a small fraction of excited molecules are expected to form the naphthalene–biphenyl exciplex.[13]

While these observations do not constitute unequivocal proof, they collectively provide compelling evidence that the 430 nm band arises from the naphthalene–biphenyl exciplex. Future confirmation via complementary techniques, such as laser induced fluorescence lifetimes, time-resolved fluorescence or excitation spectroscopy, will serve to further solidify this assignment.

Acknowledgment

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References

1. C.C. Riba, H. Chung, K.A. Martin and A.M. Nishimura, *JUCR*, **2016**, 15, 36-39.
2. H. Chung, C.C. Riba, K.A. Martin and A.M. Nishimura, *JUCR*, **2016**, 15, 105-109.
3. Z.I. Shih, B.D. Fonda, K.A. Martin and A.M. Nishimura, JUCR, **2018**, 17, 39-42.
4. S.C. Rosenhagen, C.C. Tran and A.M. Nishimura, *JUCR*, **2021**, 20, 34-37.
5. S.C. Rosenhagen, C.C. Tran and A.M. Nishimura, *JUCR*, **2021**, 20, 63-67.
6. N.M. Bond, B.P. Dionisio, A. Gillette, C.Y. Kim, A.T. Littlejohn, S.C. Rosenhagen, C.C. Tran and A.M. Nishimura, *JUCR*, **2022**, 21, 44-47.
7. N.M. Bond and A.M. Nishimura, *JUCR*, **2022**, 21, 44-47.
8. V. Kragelund, B. Bush, M. Smith and A.M. Nishimura, *JUCR*, **2026**, 25, 45-53.
9. B. Bush, M. Smith, V. Kraglund and A.M. Nishimura, *JUCR*, **2026**, 25, 54-61

10. M. Smith, V. Kraglund B. Bush, and A.M. Nishimura, *JUCR*, **2026**, 25, 65-72
11. M.K. Condie, B.D. Fonda, Z.E. Moreau and A.M. Nishimura, *Thin Solid Films*, **2020**, 697, 137823-137828.
12. M.K. Condie, C. Kim, Z.E. Moreau, B. Dionisio, K. Nili, J. Francis, C. Tran, S. Nakaoka and A.M. Nishimura, *JUCR*, **2020**, 19, 14-17.
13. J.B. Birks. *Photophysics of Aromatic Molecules*, John Wiley & Sons Ltd., New York, NY (**1970**), pp. 301-370.

Supplemental Materials

Trilayer with biphenyl, cyclohexane in the middle and naphthalene

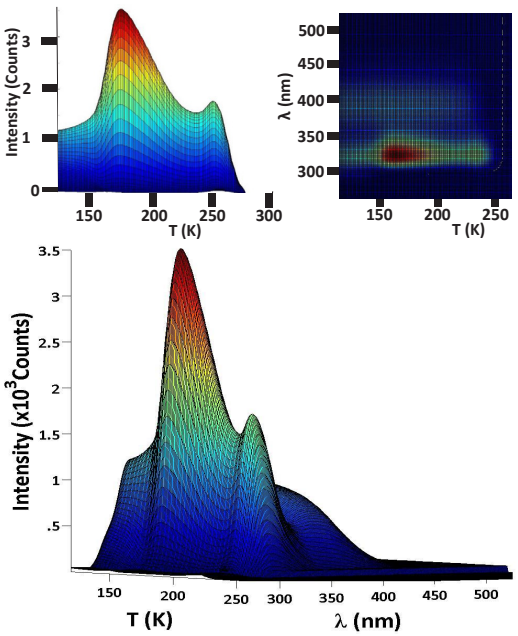

Figure S1. Wavelength-resolved TPD of trilayer consisting of naphthalene with $\Theta_{naphthalene}$ = 43ML, a middle layer of cyclohexane with $\Theta_{cyclohexane}$ = 35ML, with an overlayer of biphenyl with $\Theta_{biphenyl}$ = 61ML. Left inset: fluorescence intensity vs T during the TPD. Right inset: top view.

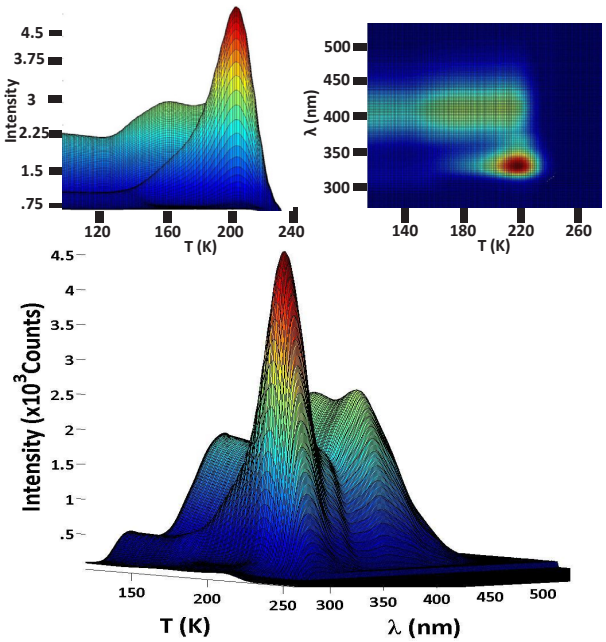

Figure S2. Wavelength-resolved TPD of trilayer consisting of biphenyl with $\Theta_{biphenyl}$ = 72 ML a middle layer of cyclohexane with $\Theta_{cyclohexane}$ = 191 ML, , with an overlayer of naphthalene with $\Theta_{naphthalene}$ = 74 ML. Left inset: fluorescence intensity vs T during the TPD. Right inset: top view.

overlayer: S1-S2.

Shown in Figure S1 is the wavelength-resolved TPD plot of the trilayer formed by vapor depositing naphthalen, followed by a middle layer of cyclohexane and finally the overlayer of biphenyl. In Figure S2 are shown the wavelength-resolved TPD plots of the the trilayer consisting of biphenyl, cyclohexane and naphthalene on the very top.

Deconvolution of the excimer-exciplex peaks: S3.

Reasonable fit of two gaussian curves to explain the excimer and exciplex peaks. The exciplex centered at 430 nm with a FWHM of 70 nm and contributed 35% of the envelope.

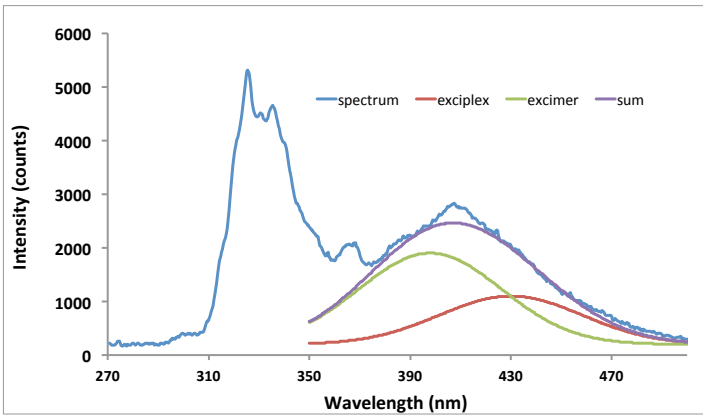

Figure S3. Curve fit of a slice of average from 200-210 K of Figure 8 in blue. The naphthalene excimer is modeled in green with λ_{max} = 398 nm. The red plot is the exciplex withλ_{max} 430 nm with a FWHM of 70 nm. The latter contributed about 35% to the total intensity, modeled here by the purple curve.