## **Supporting Information for:**

## Using Molecular Vibrations to Probe Exciton Delocalization in Films of Perylene Diimides

## with Ultrafast Mid-IR Spectroscopy

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## Section S1: Synthesis of *N*,*N*'-Bis(3-pentyl)perylene-3,4,9,10-bis(dicarboximide)

Molecule **1** was synthesized according to the procedure outlined by Handa *et al.*<sup>1</sup> After synthesis the molecule was purified using column chromatography and zone sublimation. Figure S1 shows the proton NMR spectrum of the solution dissolved in CDCl<sub>3</sub> and the corresponding assignments of the proton signals. The spectrum indicates that molecule **1** used for optical studies was of high purity.



**S1:** <sup>1</sup>H NMR spectrum of molecule **1** in CDCl<sub>3</sub> with corresponding assignments for the signals.

## Section S2: Photographs of Spray-cast Films

Figure S2 shows images of spray coated films of molecules **1** and **2**. The Penn State logo which appears in the images is behind the films to demonstrate the optical quality. Films of similar quality were spray-cast on  $CaF_2$  substrates for ultrafast measurements or pre-patterned FTO substrates for electro-absorption spectroscopy measurements.



S2: Images of PDI films spray-cast from CHCl<sub>3</sub>

#### Section S3: Evidence for Weak Ground State Interactions in Solutions of Molecule 1

To support the claim that our solutions of **1** do not significantly aggregate in chloroform up to 40 mM concentration, we measured UV-visible absorption spectra appearing in Figure 1a of the main text. We also measured FTIR spectra of the carbonyl and C-C ring modes of the perylene cores. If the molecules of 1 interacted electronically in the ground state, then changes in electronic absorption spectra and the vibrational line shapes, intensities, and peak positions would have been observed. Such changes are observed most clearly by comparing the intensity pattern of the vibrational features in the 1750 - 1550 cm<sup>-1</sup> region in the FTIR spectra films of molecules 1 and 2 in Figure S5 versus those appearing below. No such spectral changes are observed here as the concentration of the solutions increased up to 40 mM, supporting the conclusion that the solutions were comprised largely of isolated, non-interacting monomers. FTIR spectra were measured using a Agilent, Varian FTS 7000 spectrometer (Santa Clara, CA) and collected using Digilab software. The 95 mM sample, which we have identified as having ground state interactions through Uv-Vis spectroscopy in the main text of the paper has a similar FTIR spectrum as the lower concentrations which are non-interacting. This data suggests that Uv-Vis spectroscopy may be more sensitive to ground state interactions or the interactions observed in Uv-Vis for the 95 mM solution do not affect the C-C ring, or carbonyl vibrational modes for these PDI molecules.



**S3:** FTIR spectrum for molecule **1** in CHCl<sub>3</sub>. Significant spectral changes are not observed which indicates that significant electronic coupling in the ground state is not occurring.

### Section S4: Global Target Analysis to Identify Intermolecular Coordinate Coupled

#### **Vibrational Modes**

Glotaran software was used to unambiguously identify intermolecular coordinate coupled (ICC) vibrational modes in solutions of molecule 1.<sup>2</sup> Figure S4a shows the species associated spectra (SAS) for concentrations between 2 mM and 40 mM. A simple model was used to simultaneously fit the spectra and kinetics as depicted in Figure S4b. The model describes diffusion controlled excimer formation, followed by relaxation to the ground state. A 2x2 matrix



**S4:** (a) Species associated spectra for the monomer and excimer in molecule 1 solutions at varying concentrations from global target analysis performed using Glotaran software. (b) Model used to calculate the species associated spectra and format the 2x2 matrix in Glotaran.

was used to produce the two species associated spectra which are sufficient to accurately fit the entire dataset for all concentrations measured. The SAS of the monomer identifies non coupled vibrational frequencies and is characteristic of isolated molecules in solution. The Excimer SAS identifies the vibrational feature at ~1525 cm<sup>-1</sup> as an ICC mode which is spectroscopically distinct from other vibrational features in the spectra. The excimer SAS also identifies other ICC modes which are complicated by overlapping features.

## Section S5: FTIR Spectra of Spray-cast Films

The FTIR spectra of spray cast films on CaF<sub>2</sub> are provided for reference and show similar vibrational signatures. All FTIR spectra were measured using an Agilent, Varian FTS 7000 spectrometer (Santa Clara, CA) and collected using Digilab software.



**S5:** FTIR spectrum for molecule **1** and molecule **2** spray-cast films on CaF<sub>2</sub> windows

#### Section S6: Interpretation of XRD Measurements on Thin Film Samples

In addition to Bragg-Brentano X-ray diffraction patterns presented in the main text, GIXRD measurments were conducted and are shown in **Figure S6**. Included in the figure are the measured powder data and the calculated powder diffraction patterns that also appear in **Figure 4**. The powder measurements are in close agreement with the powder diffraction pattern calculated from published crystallographic information files using Mercury software.<sup>3-5</sup> In general, while there can be small local variation in the stacking and tilt of molecules, the similarities between the grazing incidence and Bragg-Brentano to the powder and simulated data suggest that they have similar unit cells and likely similar packing as a result. If large deviations in d-spacing or 2-theta in the Bragg-Brentano data were observed (~1-2°), then possible polymorph formation could be considered due to large changes in the lattice parameters.



**Figure S6:** Comparison of grazing incidence X-ray diffraction, measured Bragg-Brentano powder X-ray diffraction and calculated powder diffraction data for **(a)** molecule **1** and **(b)** molecule **2** 

However, such deviations are not observed. For the data presented in **Figure S6**, the absolute peak positions for the grazing incidence data cannot be determined; however, the Bragg-Brentano data in **Figure 4** satisfies the Bragg condition and can be used in that manner. The data confirm that the expected planes are present in the sample.

For molecule **1**, the Bragg-Brentano data (**Figure 4**) displays that there is orientation in the molecule as evidenced by the loss of many of the peaks associated with the plane of the PDI core. This indicates that the molecules are stacking perpendicular to the plane of the PDI core along the (200), (002), and (20-2) planes. As PDI molecules stack tilted to the surface with end



**S7:** Selected planes showing compound orientation on the surface and intermolecular stacking in molecule **1**.

groups in contact with the surface, the peaks present give an indication that rotation is occurring. Should molecular rotation not be occurring, one would expect that either (h00) or (001) to be present which correspond to cores extending vertically away from the substrate. However, a (20-2) peak is also observed which is depicted above as a plane between two partially tilted molecules. Partial rotation likely increases unfavorable stacking along the PDI core allowing the retention of its relative intensity compared to (200). In the grazing incidence diffraction pattern, there are many additional reflections not observed in Bragg-Brentano which are normal to the plane of the PDI core. Specifically, the high angle reflections correspond to the tilt and layering as seen above with the (221) plane. In comparison to the powder and simulated data, most of the peaks are preserved, supporting the conclusion that not only is the symmetry of the rotation retained, but also the molecular packing.

For molecule **2**, the same orientational frustration does not exist based on the molecular packing when considering surface orientation because the slip stacking leads to the end groups aligning in the same direction. Therefore, we see significant increase in peak intensity corresponding to the planes parallel to the end groups. A good example of this is the increased relative intensity of the (010) peak compared to the (01-1) reflection when compared to the calculated pattern. This is significant because the (01-1) corresponds to a plane closer to the length of the PDI whereas (010) would enable aligning the hydrocarbon end to the surface, as seen below. In terms of slip stacking versus other possible molecular packing, the (104) and (01-1) peaks which correspond to rows of PDI molecules (**Figure S8**) fall on top of the calculated



**S8:** Selected planes showing compound orientation on the surface and intermolecular stacking in molecule 2.

and powder pattern. These observations give us confidence that though there is significant ordering to the substrate, the consistent peak positions in Bragg-Brentano with the calculated pattern mean that planes of molecules in the thin film lie in the same location as in the single crystal data from literature.<sup>3-5</sup>

#### Section S7: Measured Absorption and Emission Spectra for PDI Spray-cast Films

We measure the ultraviolet-visible (UV-Vis) and fluorescence spectra of films of **1** and **2** to characterize their absorption and emission properties. The Uv-Vis of the films was measured in a Perkin Elmer Lambda 950 Uv-Vis-NIR spectrophotometer (Waltham, MA) using an integration sphere to correct for sample scatter. Photoluminescence of the films was collected from the front surface using a frequency-doubled Nd: YAG laser (Surelite I, Continuum; Santa Clara, CA) as an excitation source with an energy density of ~75  $\mu$ J/cm<sup>2</sup>. The film emission was detected using a 70 MHz InGaAs photodiode (DET10N,Thorlabs; Newton, NJ). The instrument response time for these measurements was ~10 ns. The data in **Figure S9** highlight the difference between the electronic states of molecule **1** and **2**.



**S9:** Normalized absorption and photoluminescence spectra for films of molecules **1** and **2**. Absorption spectra are corrected for scatter.

# <u>Section S8</u>: Complete Ultrafast Mid-IR Transient Absorption Spectra for PDI Spray-cast Films

Although we highlight the usefulness of the C-C stretch region in the ultrafast transient absorption spectra, the entire C-C ring mode and carbonyl vibrational regions were measured. The full spectra are given in **Figure S10**. These spectra highlight the issue of overlapping features in the spectral regions we chose not to interpret and exhibit the quality of data that was collected.



S10: Full measured ultrafast transient absorption vibrational region for films of molecule 1 and 2

## <u>Section S9</u>: Degradation of Thin Film Samples Exposed to the Ultrafast Experimental Conditions

For our ultrafast measurements on thin films of molecules 1 and 2, the pump laser had an incident energy density of ~120  $\mu$ J/cm<sup>2</sup>. Figure 11a depicts the results of control experiments measured at the peak of the ICC mode at 1530 cm<sup>-1</sup>. We performed these measurements to determine the length of time over which transient absorption measurements could be made under these conditions before degradation of the samples was observed. The data show that degradation in the signal amplitude was not observed within the first four scans over the time delays recorded in the measurements. After eight scans, some degradation was observed, which is apparent as a decrease in the signal observed for the ICC mode measured at 1530 cm<sup>-1</sup>. To systematically avoid possible effects of this degradation process, we recorded only two scans over the measured time delays at any single spot in the sample. After every two scans, the sample was moved so that the pump and probe beams interacted with a fresh region of the sample. Because we use an infrared array detector, these scans enabled us to collect 32 probe frequencies simultaneously within the measured vibrational spectra. The separate spectral regions were then connected to yield the total measure infrared region. Both molecule 1 and 2 are shown to remain stable under our laser irradiation for two scans as evidenced by Figure S11.



**S11:** Transient absorption decays of the ICC modes measured for **(a)** molecule **2** at 1530 cm<sup>-1</sup>. The sequential scans demonstrate the absence of a change in the signal amplitude for up to eight scans. At scan eight a decrease in amplitude is observed which continually decreases on each additional scan. Averaging only two scans eliminates the chance of biasing our measured results through degradation in thin films of molecule **1** and **(b)** molecule **2** as evidenced by the absence of a decreased intensity of the ICC vibrational mode at 1525 cm<sup>-1</sup>.

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