

Defects Cause the Tail in the Luminescence Spectrum of a Crystalline Tetracene Derivative

R. Eric McAnally,[†] Jon A. Bender,[‡] Laura Estergreen,[†] Ralf Haiges,[†] Stephen E. Bradforth,[†] Jahan M. Dawlaty,[†] Sean T. Roberts,[‡] and Aaron S. Rury^{*,¶}

Department of Chemistry, University of Southern California, Los Angeles, CA, USA 90089, Department of Chemistry, University of Texas at Austin, Austin, TX, USA 78712, and Department of Chemistry, Wayne State University, Detroit, MI, USA 48202

E-mail: arury@chem.wayne.edu

^{*}To whom correspondence should be addressed

[†]Department of Chemistry, University of Southern California, Los Angeles, CA, USA 90089

[‡]Department of Chemistry, University of Texas at Austin, Austin, TX, USA 78712

[¶]Department of Chemistry, Wayne State University, Detroit, MI, USA 48202

Comparison of Vibrational Coherence Spectrum to Probe Pulse Spectrum

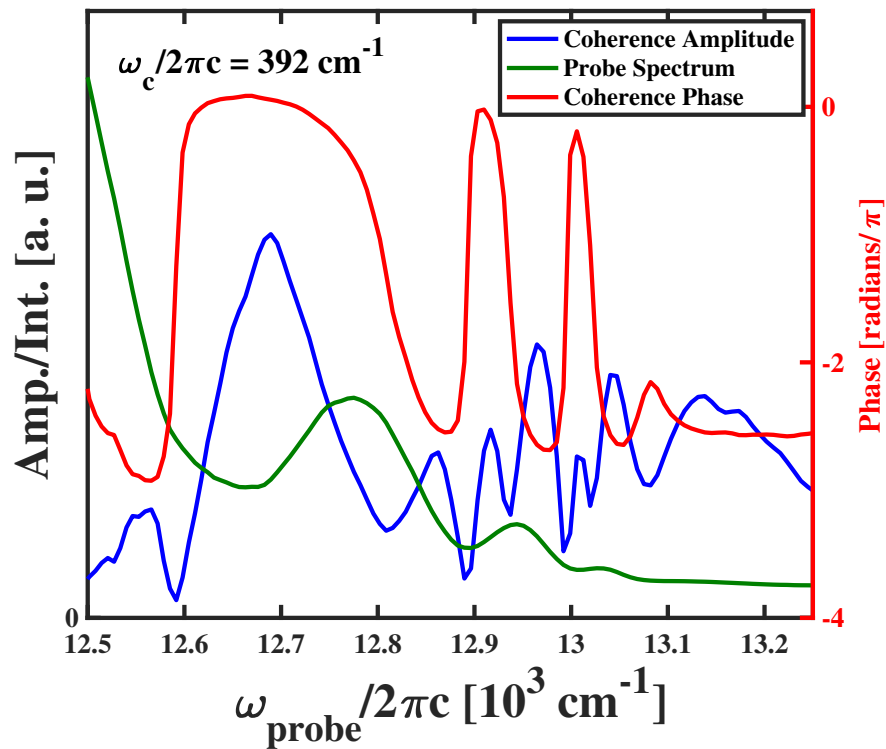


Figure S1: Comparison of the spectral dependence of the amplitude (blue) and phase (red) of a vibrational coherence found at 392 cm^{-1} to the spectral dependence of the probe pulse used to measure the coherence. This comparison shows the structure of the coherence spectrum does not derive from the structure of the probe pulse.

Figure S1 compares the spectrum of the probe pulse used in the ultrafast nonlinear spectroscopy measurements to the vibrational coherence spectrum (VCS) of the feature found at 392 cm^{-1} using the Fourier analysis described in the text. Upon inspection of these spectra one sees that while the probe pulse spectrum possesses structure, it does not resemble the structure observed in the VCS. This solidifies our conclusion that the structure of the VCS report the coupling of difference vibrational coherences to absorptive transitions in the band-gap of DPT.

Comparison of Vibrational Coherence Spectrum to Photoluminescence Spectral Tail

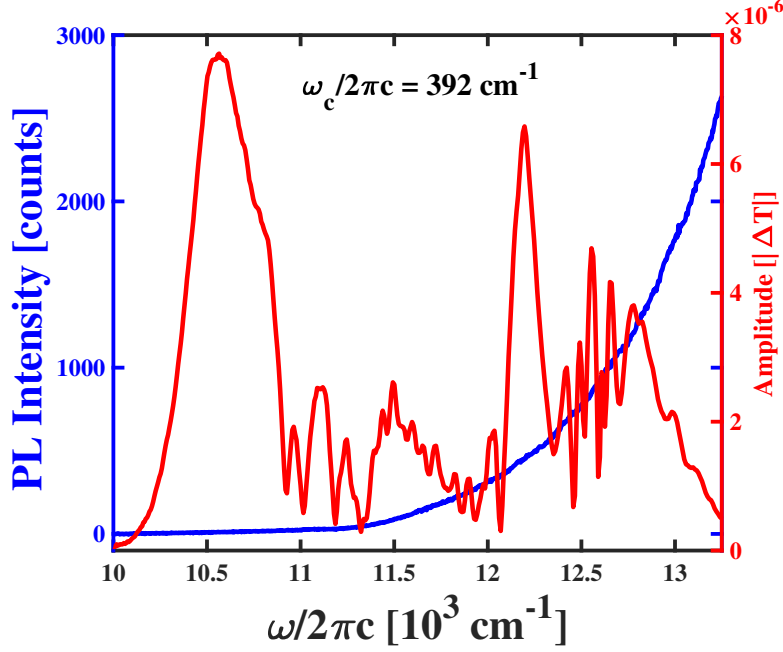


Figure S2: Comparison of the low energy photoluminescence spectra of a DPT single crystal excited at 18800 cm^{-1} to the amplitude of the 392 cm^{-1} coherence.

Figure S2 shows a comparison of the low energy tail emitted by a single crystal of DPT following excitation at 18800 cm^{-1} across the entire band of frequencies present in the light pulse used to probe a DPT single crystal following impulsive stimulated Raman scattering excitation at 7150 cm^{-1} . This comparison shows anti-peaks that denote the presence of absorptive transitions only appear in spectral regions in which we measure photoluminescence emission from the sample. In addition, we observe a large amplitude feature peaked near 10500 cm^{-1} with no anti-peaks in that spectral region. This feature indicates that the vibrational coherence at 392 cm^{-1} only couples to the real part of the dielectric function of DPT, as would be expected in the absence of absorptive transitions in this region. While there is some ambiguity in the baseline of the PL spectrum due to the finite integration time of the measurement, the properties of the VCS indicate the baseline should begin just below

11000 cm^{-1} .

Absorption of Impurity Bands

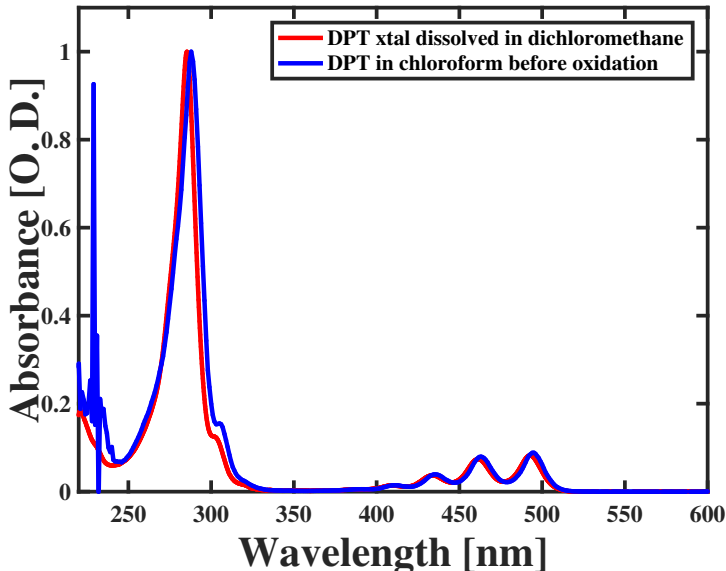


Figure S3: Comparison of the absorption spectrum of dissolved single crystals of 5,12-diphenyl tetracene (DPT) with unknown impurity levels to that of a known pristine DPT solution sample. This comparison shows that the crystalline samples do not contain a sizable population of oxidized DPT molecules that could affect the interpretation of the spectroscopic results of the main manuscript text.

The predominant impurity found in previous reports of the optical spectra of DPT corresponded to an oxidized form of the molecule. As shown by Mastron *et al*, this impurity leads to a decrease in the vibronic absorption of the pristine molecule when solid samples are dissolved in solution.¹ To test of the presence of this dominant impurity in the crystalline samples used for the present study, we measured the absorption spectrum of single crystals dissolved in dichloromethane and compared them to known pure solution samples of DPT in chloroform. Figure S3 demonstrates this comparison shows the lack of spectral features due to oxidized impurities in our crystalline samples. Specifically, the presence of the vibronic structure of the $S_0 \rightarrow S_1$ transition and the absence of the oxidized peak at 250 nm indicate

that our sample does not contain the oxidized form of DPT. The photoluminescence spectra of solution samples of pristine DPT do not show the presence of other impurities that emit in the region of interest in the present study, indicating impurities play at most a minor role in the observations of the main text.²

References

- (1) Mastron, J. N.; Roberts, S. T.; McAnally, R. E.; Thompson, M. E.; Bradforth, S. E. Aqueous Colloidal Acene Nanoparticles: A New Platform for Studying Singlet Fission. *J. Phys. Chem. B* **2013**, *117*, 15519–15526.
- (2) Roberts, S. T.; McAnally, R. E.; Mastron, J. N.; Webber, D. H.; Whited, M. T.; Brutchey, R. L.; Thompson, M. E.; Bradforth, S. E. Efficient Singlet Fission Discovered in a Disordered Acene Film. *J. Am. Chem. Soc.* **2012**, *134*, 6388–6400.