

Dynamics of Singlet Fission and Electron Injection in Self-Assembled Acene Monolayers on Titanium Dioxide

Electronic Supporting Information

Natalie A. Pace,^{‡ab} Dylan H. Arias,^{‡a} Devin B. Granger,^c Steven Christensen,^a John E. Anthony^c and Justin C. Johnson^{*a}

a) National Renewable Energy Laboratory, Golden, CO, USA 80401. E-mail: Justin.johnson@nrel.gov

b) Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA 80309

c) Department of Chemistry, University of Kentucky, Lexington, Kentucky, USA 40506

‡ These authors contributed equally to this work

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S1. Steady-state photoluminescence

Steady-state photoluminescence (SSPL) was measured with a Horiba Jobin Yvon Model FL-1039/40 Fluorolog, a Horiba Jobin Yvon iHR320 spectrograph, and a Horiba Jobin Yvon SPEX Instruments S.A. Group Spectrum One G35 CCD camera. A monochromatized Xe lamp was used as the excitation source.

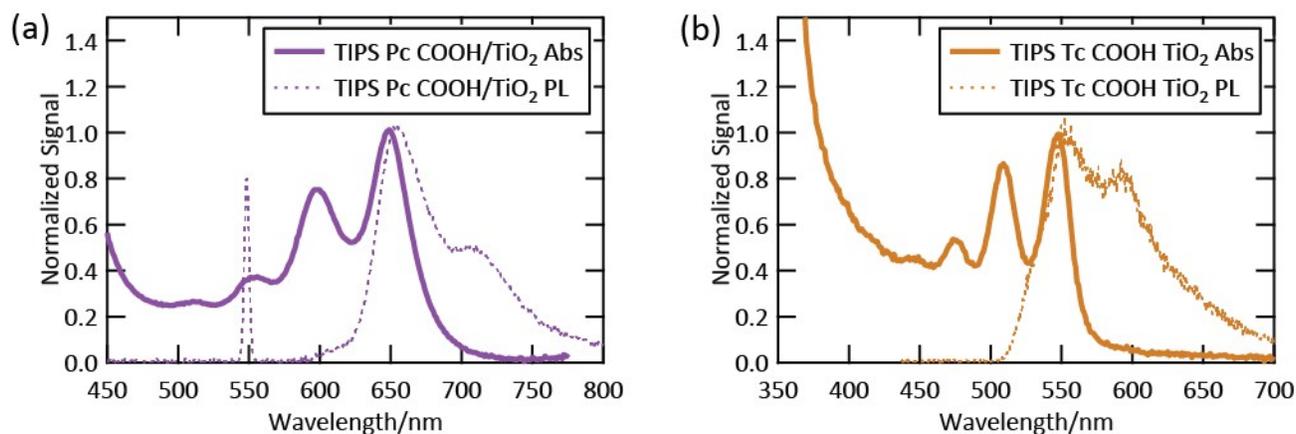


Figure S1 UV-VIS and photoluminescence spectra for (a) TIPS Pc COOH/TiO₂ and (b) TIPS Tc COOH/TiO₂.

Fig. S1 shows SSPL of both acenes linked to TiO₂. A combination of the singlet ground-state absorption and singlet emission were used to calculate S1 energies in Table 1 of the main text.

S2. Solution transient absorption

TIPS Pc and TIPS Pc COOH were dissolved in ethanol and TIPS Tc and TIPS Tc COOH were dissolved in toluene to make ~0.1-0.3 OD solutions for TA measurements. Each compound features a unimolecular decay of a single species, presumably the singlet. Each spectrum has similar features: a large singlet photoinduced absorption peaked near 450 nm, overlapping ground state bleach and stimulated emission at the 0-0 of the absorption and photoluminescence spectra, and an isolated stimulated emission feature at the 0-1 of the photoluminescence spectra (Fig. S2).

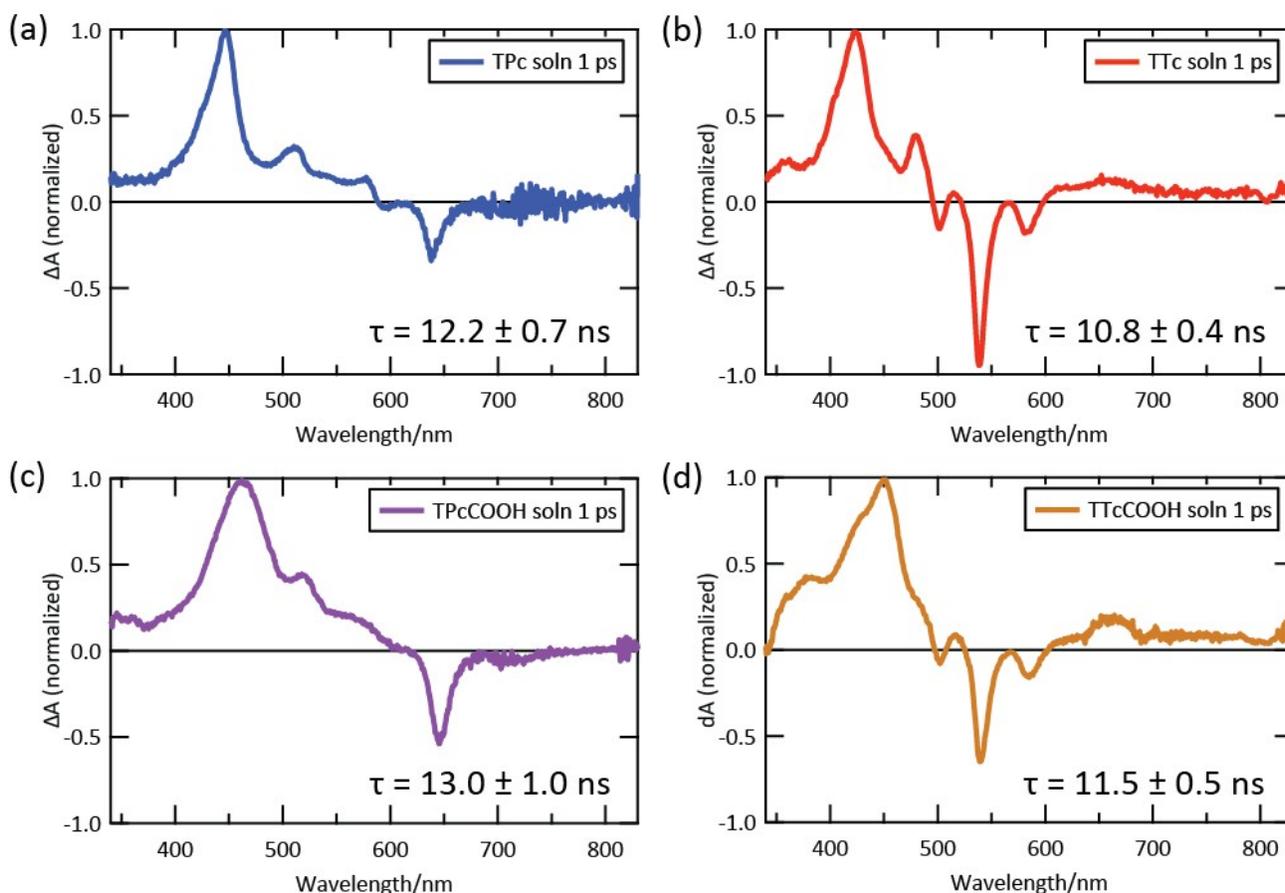


Figure S2 Solution-phase TA spectra measured at 1 ps. (a) TIPS Pc, (b) TIPS Tc, (c) TIPS Pc COOH, and (d) TIPS Tc COOH.

S3. X-ray diffraction

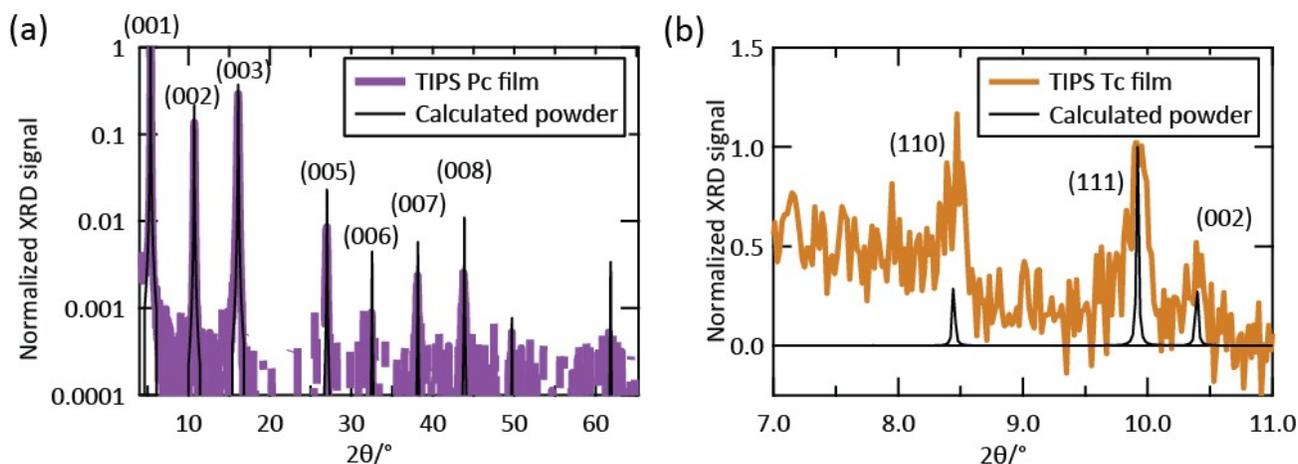


Figure S3 XRD diffraction patterns comparing thin film and calculated powder diffraction. (a) TIPS Pc. (b) TIPS Tc.

XRD data were measured using a Rigaku DMax 2500 X-ray Diffractometer operating in $\theta/2\theta$ mode using $\text{Cu-K}\alpha$ radiation (0.154 nm). The TIPS Pc film showed peaks matching the single crystal (001) to (008) diffractions (Fig. S3a).¹ This implies a highly ordered and highly oriented polycrystalline film with the c-axis approximately normal to the

substrate. On the other hand, the TIPS Tc film showed no diffraction peaks as deposited. After annealing, it showed weak diffraction matching the (110), (111), and (002) peaks from single crystal diffraction (Fig. S3b).² Not only does this imply weak geometrical order, but no preferential crystallite orientation.

S4. Film TA Global Analysis (Decay Associated Spectra)

We used global analysis to determine kinetics of singlet fission or electron injection. Specifically, we fit each two-dimensional spectrum to a linear combination of decaying exponentials where the decay times are fit globally, and the amplitudes varies as a function of wavelength. This generates decay associated spectra (DAS), allowing us to ascribe decay or growth times to spectral features present in the raw data. However, it should be noted these do not represent excited-state species. We are simply correlating spectral features in the raw data, DAS, and SEC cation or triplet sensitized spectra.

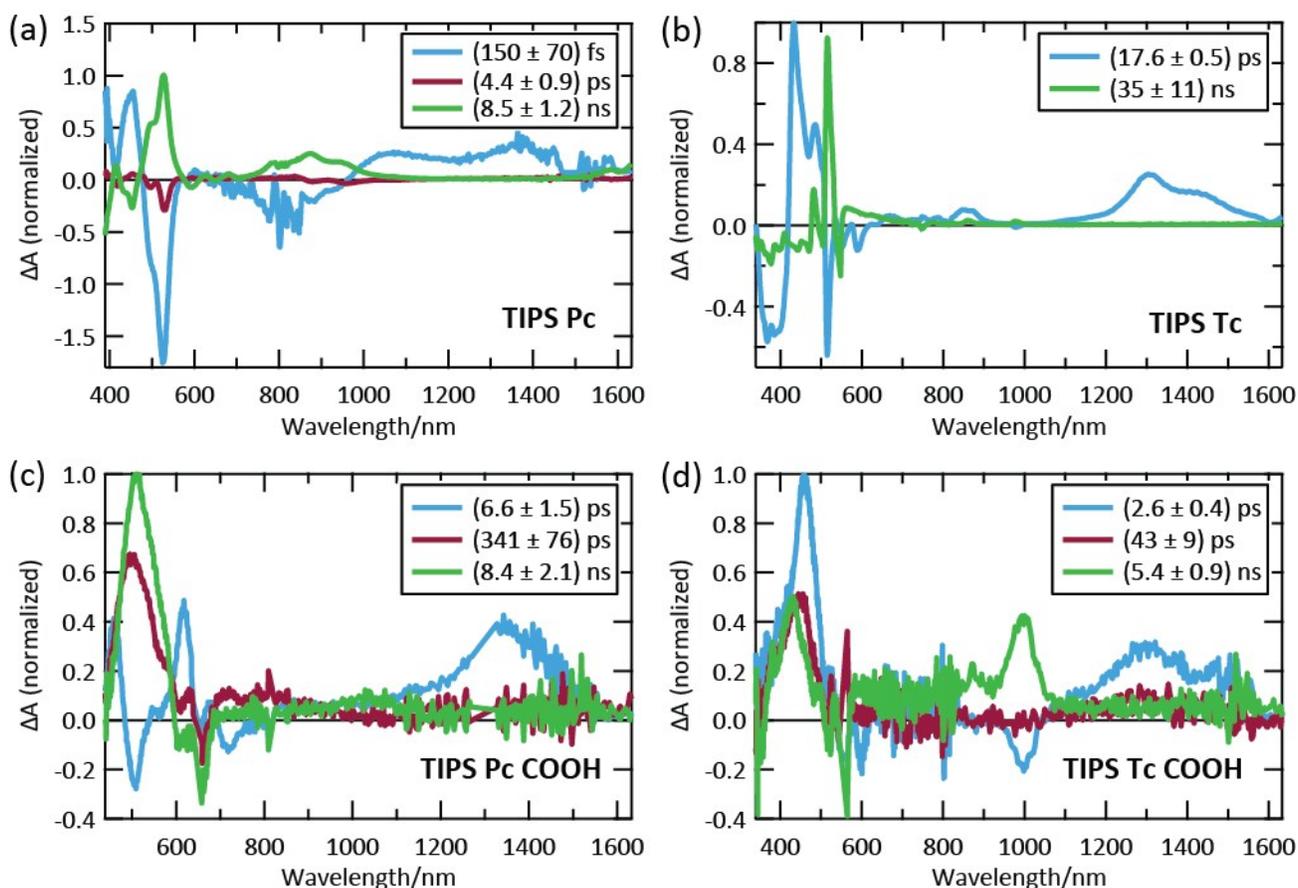


Figure S4 Decay associated spectra for (a) TIPS Pc film, (b) TIPS Tc film, (c) TIPS Pc COOH/TiO₂, and (d) TIPS Tc COOH/TiO₂.

Fig. S4 shows the DAS for all four films studied. DAS with the shortest lifetime were taken to represent a mix of singlet decay and triplet or cation growth. In TIPS Pc (Fig. S4a), the 4.4 ps DAS features a few small growth features on the triplet PIA peaked near 515 nm and 900 nm, similar to that seen by Pensack et al.³ The third DAS represents the decay of the features back to the ground state. In TIPS Tc films, there are only two DAS: the first (17.6 ps) represents singlet decay and triplet growth, and the second (35 ns) correlates with subsequent triplet decay. TIPS Pc COOH/TiO₂ features three DAS spectra: an initial singlet decay and triplet growth (6.6 ps) and subsequent minor relaxation processes that involve subtle shifts of the triplet features and finally decay of the triplet to the ground state. TIPS Tc COOH/TiO₂ also requires three DAS for fitting the data: initial singlet decay and cation growth (2.6 ps); subsequent

relaxation and subtle shifts possibly related to cation relaxation or perhaps singlet fission that is partially hidden and overlapping with cation kinetics (43 ps); and decay back to the ground state (5.4 ns).

S5. Kinetics of TIPS Tc COOH/Al₂O₃/TiO₂ System

The primary kinetics of the singlet PIA feature (Fig. S5a; Fig. 6a) diverge from the kinetics of the TIPS Tc COOH cation PIA feature (Fig. S5b, Fig. 6b) in the TIPS Tc COOH/Al₂O₃/TiO₂ system. Both kinetics can be fit with single exponentials, where the kinetic at 1215 nm decays in 40 ± 10 ps, and the kinetic at 946 nm rises with a time constant of 250 ± 60 fs (which is approximately the instrument response).

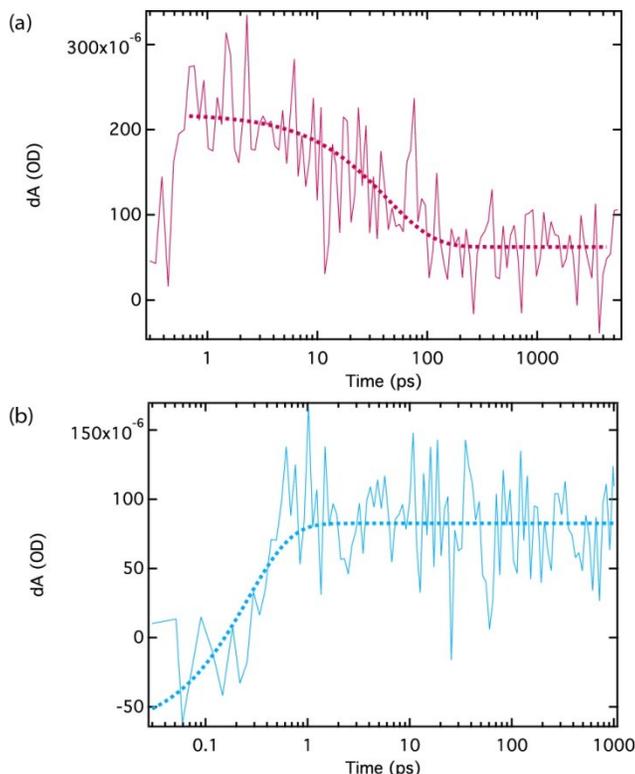


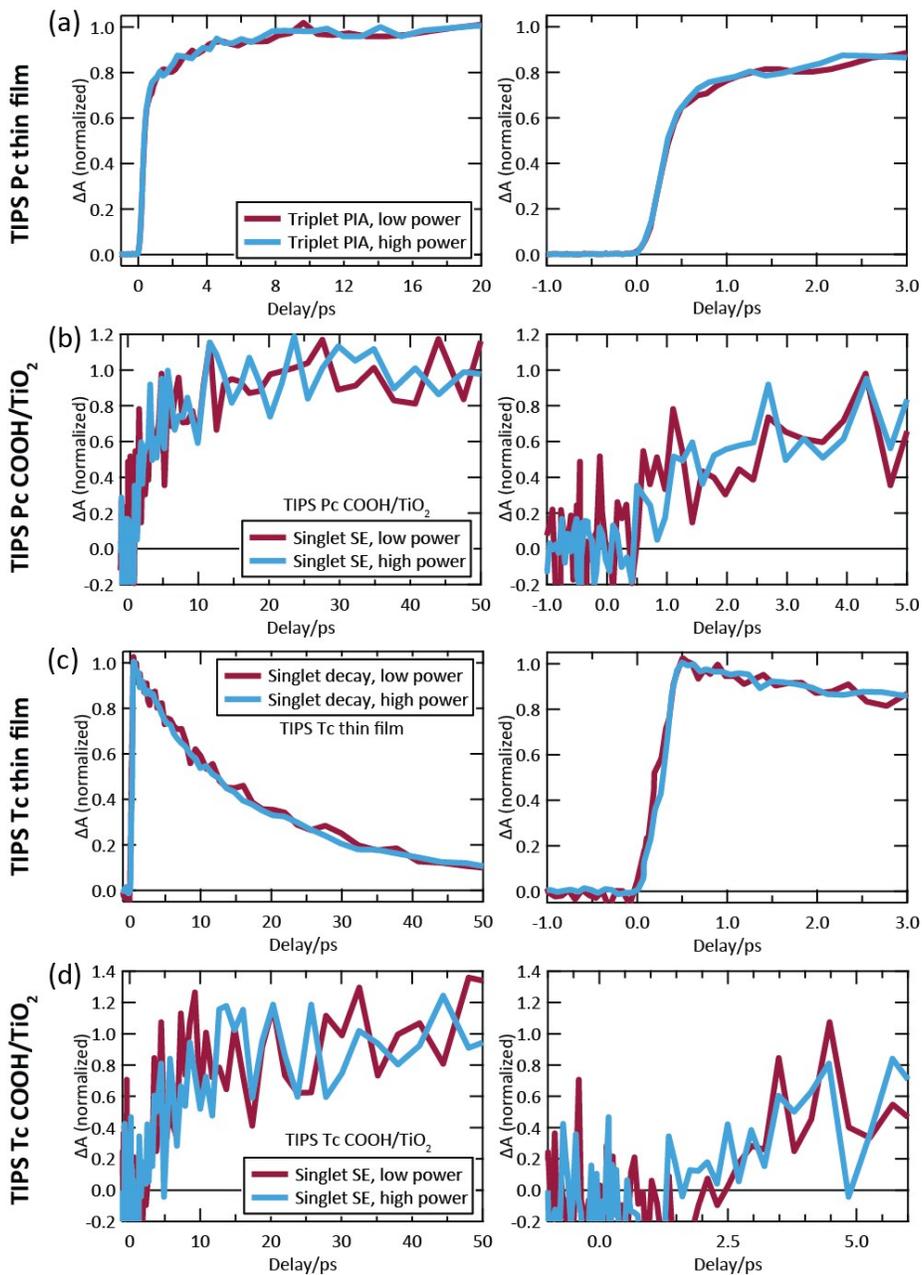
Figure S5 Kinetics (solid lines) and fits (dotted lines) of (a) Singlet PIA feature (1215 nm) and (b) TIPS Tc COOH cation PIA feature (946 nm).

Since the cation feature does not rise further within the time window, the measured singlet decay time likely corresponds exclusively to the singlet fission process. The lack of additional rise in the location of the cation PIA implies generated triplets do not contribute to charge generation. Since the cation and singlet kinetics are distinct from each other in this time window, the small population of charges generated is probably a result of Al₂O₃ film heterogeneity, where some small subset of TIPS Tc COOH molecules experience little barrier to charge injection. The fast rise in the signal at 1215 nm is probably due to singlet PIA that is broadly spread across the NIR (see Fig. 4d and Fig. 6a in main text); while the signal left at long times, after the singlet has decayed, is probably due to the small population of residual charges.

S6. Fluence-dependent and early-time TA

In Fig. S6 we display plots of low and high power (high power $\sim 3 \times$ low power in each film) kinetic data for each film demonstrating fluence-independence. We include both long time (tens of ps, Fig. S6 left) to show data after singlet fission or charge injection; and short time (< 5 ps, Fig. S6 right) to show the lack of sub-ps dynamics in all samples except TIPS Pc thin films. For TIPS Pc (Fig. S6a), we show kinetics of the triplet PIA near 520 nm, demonstrating the sub-ps rise of the PIA and secondary 4-5 ps rise. For TIPS Pc COOH/TiO₂, we show the decay of SE, which appears as a

rise into a triplet PIA feature (Fig. S6b). For TIPS Tc films we show near-isolated singlet decay kinetics taken at 477 nm as the triplet spectrum has a node near 477 nm (Fig. S6c). For TIPS Tc COOH/TiO₂ we show stimulated emission, similar to TIPS Pc COOH/TiO₂ (Fig. S6d).



References

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