Supporting Information for:

Singlet Fission in 9,10-Bis(phenylethynyl)anthracene Thin Films

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BPEA powder X-ray diffraction (PXRD) analysis. BPEA polycrystalline powder was purchased from Sigma Aldrich and PXRD data were collected at room temperature on a STOE-STADIMP powder diffractometer equipped with an asymmetric curved Germanium monochromator (CuK α 1 radiation, $\lambda = 1.54056$ Å) and one-dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). The line focused Cu X-ray tube was operated at 40 kV and 40 mA. The pristine powder was packed in a 3 mm metallic mask and sandwiched between two layers of polyimide tape. The instrument was calibrated against a NIST Silicon standard (640d) prior to the measurements. Rietveld analysis¹ was performed using the JANA2006² software. From the analysis (Figure S1), there is 40.10(2) % of Pbcn and 59.90(2) % of C2/c polymorphs.



Figure S1. The experimental (black) and calculated PXRD pattern of BPEA polycrystalline powder and peak positions of polymorph Pbcn (blue) and C2/c (magenta).

Film preparation details. Thin film samples were deposited on sapphire substrates at room temperature at a rate of 0.2 Å/s in a vacuum thermal evaporator (Denton Vacuum DV502-A), followed by solvent-vapor annealing using dichloromethane (DCM) overnight. A heating plate inside the N_2 glovebox was used to thermally anneal the films for 3 hrs at 120 °C; the films were then cooled overnight prior to characterization. Film thicknesses were measured with a Veeco

Dektak 150 surface profilometer with a 5.0 μ m diameter stylus to be 170 \pm 10 nm, and 310 \pm 30 nm for the solvent annealed and thermally annealed films, respectively.

Quantitative analysis of polymorphs in the solvent annealed film. A small amount of powders was scrapped off the annealed film and measured at room temperature on a Bruker Prospector system equipped with the micro-focused X-ray tube and MX optics. The same analysis method with the polycrystalline powder (Figure S1) was used; there is 38.8 ± 0.5 % of Pbcn and 61.2 ± 0.5 % of C2/c polymorphs, which is very similar to the results obtained for the bulk powder.

Steady state spectroscopy. Steady state absorbance of the solution sample was measured using Shimadzu UV-1800 spectrometer and scatter-corrected absorbance of film samples were measured using Shimadzu UV-3600 UV/vis/NIR spectrometer equipped with an integrating sphere. Steady state fluorescence spectra of solution and film samples were measured in the front face mode with a HORIBA Nanolog spectrofluorimeter equipped with an integrating sphere (Horiba Quanta - φ) for absolute fluorescence quantum yield determination.

Femtosecond transient absorption (fsTA) spectroscopy at a 1 kHz repetition rate. Femtosecond transient absorption spectroscopy (fsTA) experiments were conducted using a regeneratively-amplified Ti:sapphire laser system operating at 828 nm and a 1 kHz repetition rate as previously described.³ Solution samples were prepared in a 2 mm path length glass cuvette and degassed with three freeze-pump-thaw cycles. Film samples were placed under vacuum in a cryostat (VPF-100, Janis Research, ~3 x 10⁻⁴ Torr) to be in an oxygen free environment. The pump spot size at the sample position was 0.4 mm diameter at the sample and the pump fluence was 0.8 μ J/pulse, resulting in the excitation density of 7.8 x 10¹⁹ cm⁻³ for the solvent-annealed film and 4.3 x 10¹⁹ cm⁻³ for the thermally annealed film. Steady-state and transient spectroscopy of solution-phase BPEA.



Figure S2. (a) The absorption and emission spectra of BPEA in CH_2Cl_2 to determine the S₁ energy (2.64 eV). (b) The fsTA spectra of BPEA in CH_2Cl_2 give the singlet excited state lifetime as 3.17 ± 0.02 ns.

Triplet sensitization using palladium octabutoxyphthalocyanine (PdPc(OBu)₈). To determine the triplet spectrum of BPEA in the thin film, a CH₂Cl₂ solution containing BPEA and PdPc(OBu)₈ (95:5 weight ratio) at a concentration of 10 mg/mL was spin-coated on a glass substrate at 1500 rpm. Figure S3 shows the steady state absorbance of the sensitized film. The fsTA spectra of the sensitized film were then acquired following selective excitation of PdPc(OBu)₈ at 720 nm. Rapid intersystem crossing populates ^{3*}PdPc(OBu)₈, which then energy transfers to ^{3*}BPEA. The sensitized spectrum (Figure S4a) is in good agreement with the spectrum of the BPEA thin film excited at 500 nm (Figure S4b). Here, BPEA thin film was excited at 500 nm to compare the triplet spectrum.



Figure S3. Steady-state absorbance of the $PdPc(OBu)_8$ doped BPEA spin-coated film where the bands at 350-550 nm result from BPEA and the band from 550-850 nm results from $PdPc(OBu)_8$.



Figure S4. FsTA spectra of (a) the sensitized film excited at 720 nm, and (b) a BPEA thin film excited at 500 nm



Figure S5. (a) fsTA spectra of a drop-casted PdPc(OBu)₈ film excited at 720 nm. (b) Normalized kinetics of the neat PdPc(OBu)₈ and sensitized BPEA films at 461 nm, following selective excitation of the phthalocyanine at 720 nm.

Delayed fluorescence from the solvent annealed BPEA film. Time-correlated photon counting (TCSPC, Horiba Nanolog) was used to observe the weakly emitting delayed fluorescence of the solvent annealed BPEA film. The film sample was placed under vacuum in a cryostat (VPF-100, Janis Research, \sim 3 x 10⁻⁴ Torr) and monitored for the first 14 µs following excitation at 370 nm. (Figure S5).



Figure S6. (a) Spectra at specific time points and (b) intensity profile at 540 nm showing delayed emission of the solvent-annealed film during the 10 µs time window.

Singlet Oxygen Emission

Kinetic model for 1 kHz fsTA data analysis.

The global fitting procedures have been described in detail previously.⁴ The fsTA data of the solvent-annealed films (Figure 3A) acquired here were globally fit to the following kinetic model:

$$\frac{d[S_{\rm A}]}{dt} = -\frac{k_{SSA}^{(A)}}{2} [S_{\rm A}]^2 - k_{SFA} [S_{\rm A}]$$
(1)

$$\frac{d[S_{\rm B}]}{dt} = -\frac{k_{SSA}^{(B)}}{2} [S_{\rm B}]^2 - k_{SFB} [S_{\rm B}]$$
(2)

$$\frac{d[T_1]}{dt} = 2k_{SFA}[S_A] + 2k_{SFB}[S_B] - k_T[T_1]^2$$
(3)

where $k_{SSA}^{(A)}$ and $k_{SSA}^{(B)}$ are the singlet-singlet annihilation rate constants, and S_A and S_B are two different excited singlet populations resulting from the two different polymorphs in the film. k_{T} is



Figure S7. Steady-state singlet oxygen emission spectrum recorded using HORIBA Nanolog spectrofluorimeter coupled to NIR-PMT 900-1700 nm detector upon excitation of a BPEA solvent-annealed film excited at 414 nm.

the triplet-triplet annihilation rate constant. Initial populations of each singlet species (0.6 and 0.4, respectively) were set according to the relative values determined by PXRD. Fitting the data to the solutions of the differential equations (eqns. 1-3) of three different measurements and averaging them yields the two different SF rate constants corresponding to S_A and S_B, respectively are $k_{SFA} = (90 \pm 30 \text{ ps})^{-1}$ and $k_{SFB} = (480 \pm 40 \text{ ps})^{-1}$, indicating that one polymorph undergoes faster SF than the other. The faster rate extracted for species A ([S_A]₀ = 0.6) and the slower rate for species B

 $([S_B]_0 = 0.4)$ is consistent with the assignments of the SF dynamics to the two populations in the main text. The two singlet-singlet annihilation rate constants, $k_{SSA}^{(A)}$ and $k_{SSA}^{(B)}$, are $(8.3 \pm 0.7 \times 10^{-2} \text{ ps}^{-1}\Delta \text{A}^{-1})$ and $(3 \pm 1 \text{ ps}^{-1}\Delta \text{A}^{-1})$, respectively.



Figure S8. FsTA data analysis for the solvent-annealed film. (a) Globally fit kinetics at selected wavelengths. (b) Relative populations of the singlet and triplet states as a function of time.

The fsTA data of the thermally-annealed films (Figure S8) acquired here were globally fit to the following kinetic model:

$$\frac{d[S_{\rm B}]}{dt} = -\frac{k_{SSA}^{(B)}}{2} [S_{\rm B}]^2 - k_{SFB} [S_{\rm B}]$$
(4)

$$\frac{d[T_1]}{dt} = 2k_{SFB}[S_B] - k_T[T_1]^2$$
(5)

In the thermally-annealed film, there exists ~97% of Pbcn polymorph and so, there is one singlet population denoted as S_B. Solving the differential equations (eqns. 4-5) the singlet-singlet annihilation rate, $k_{SSA}^{(B)}$ and the k_{SFB} are (0.25 ± 0.06 ps⁻¹ Δ A⁻¹) and (500 ± 100 ps)⁻¹, respectively.



Figure S9. FsTA data obtained at $4.3 \times 10^{19} \text{ cm}^{-3}$ excitation density and a 1 kHz repetition rate of the thermally annealed BPEA film.

Femtosecond transient absorption (fsTA) spectroscopy at a 100 kHz repetition rate. FsTA experiments were conducted using a non-collinear optical parametric amplifier (Light-Conversion, LLC, Spirit-NOPA) pumped by an amplified Yb:KGW femtosecond laser (Spectra-Physics, Spirit-4) operating at 100 kHz as described previously to generate a 14 nJ, 414 nm, 100 fs pump pulse and a corresponding white light probe pulse.⁵ The bluer white light probe was generated after frequency doubling the fundamental to create 520 nm light and using an 8 mm long YAG crystal to generate probe light at 390-500 nm. The pump spot size at the sample position was 1.0 mm diameter resulting in the excitation density of 1 x 10¹⁷ cm⁻³. The global data fits using the kinetic



Figure S10. FsTA data obtained at 10^{17} cm⁻³ excitation density and a 100 kHz repetition rate. (a) fsTA spectrum of the solvent-annealed BPEA film; (b) the reconstructed species-associated spectra; (c) global fits to selected wavelengths; and (d) a population vs time plot obtained by global fitting to the kinetic model specified in the text.

model given by eqs 1-5 in the SI without the SSA due to the decreased excitation density are presented in Figure S9 and S10.



Figure S11. FsTA data obtained at 10^{17} cm⁻³ excitation density and a 100 kHz repetition rate. (a) fsTA spectrum of the thermally annealed BPEA film; (b) the reconstructed species-associated spectra; (c) global fits to selected wavelengths; and (d) a population vs time plot obtained by global fitting to the kinetic model specified in the text.

Picosecond time-resolved fluorescence (TRF) spectroscopy. The output of a non-collinear optical parametric amplifier (Light-Conversion, LLC, Spirit-NOPA) pumped by an amplified Yb:KGW femtosecond laser (Spectra-Physics, Spirit-4) operating at 100 kHz was used for TRF. The film samples were kept under vacuum inside a cryostat and was excited with 414 nm, ~100 fs, 1 nJ/ pulses. The TRF signal was collected using a streak camera system (Hamamatsu C4334 Streakscope), with time windows of 1 ns with an instrument response function (IRF) of 20 ps and of 5 ns with an IRF of 90 ps. Time windows of 1 and 5 ns were used. (Figures S11-S14).

The data for the solvent-annealed film (Figure S11) in a 1 ns time window was fit with a biexponential function to give $k_1 = (109 \pm 3 \text{ ps})^{-1}$) and $k_2 = (870 \pm 20 \text{ ps})^{-1}$, where the first component is attributed to the SF rate from C2/c polymorph and the second component is presumably the combined SF rate from the Pbcn polymorph and the delayed emission. The data for the solventannealed film was obtained in the longer 5 ns time window (Figure S12) to yield $k_1 = (109 \pm 4 \text{ ps})^{-1}$, $k_2 = (490 \pm 10 \text{ ps})^{-1}$), and $k_3 \gg (5 \text{ ns})^{-1}$, where the longest emission rate once again corresponds to delayed emission. The corresponding data for the thermally annealed film in the 1 ns time window (Figure S13) has $k_1 = (510 \pm 20 \text{ ps})^{-1}$) and $k_2 \gg (1 \text{ ns})^{-1}$, which is attributed to SF from the Pbcn polymorph and the delayed emission, respectively, while the data in the 5 ns time window (Figure S14) yields $k_1 = (490 \pm 10 \text{ ps})^{-1}$), and $k_2 \gg (5 \text{ ns})^{-1}$, which further differentiates the SF rate from the Pbcn polymorph and the delayed emission. The delayed fluorescence decay rate constant was obtained using a 10 µs time window (Figure S5) ($k_T = (196 \pm 5 \text{ ns } \Delta \text{A})^{-1}$).



Figure S12. (a) TRF spectrum with 1 ns time window of the solvent-annealed film and (b) wavelength fitting using a biexponential fit.



Figure S13. (a) TRF spectrum of the solvent-annealed film with 5 ns time window and (b) wavelength fitting using a triexponential fit.



Figure S14. (a) TRF spectrum of the thermally annealed film with 1 ns time window and (b) wavelength fitting using a biexponential fit.



Figure S15 (a) TRF spectrum of the thermally annealed film with 5 ns time window and (b) wavelength fitting using a biexponential fit.

Nanosecond transient absorption (nsTA) spectroscopy. The nanosecond transient absorption (nsTA) was performed with a 7 ns, 416 nm laser pulse at 10 Hz repletion rate. Details of the experiment are given elsewhere.⁶



Figure S16. nsTA spectra for the BPEA thin film excited with a 7 ns, 416 nm, 1 mJ pulse. Spectra are sampled at 2 nm increments. (a) solvent-annealed. (b) thermally-annealed.

Triplet yield calculation using the singlet depletion method.

The singlet depletion method,⁷ is based on quantifying the ground-state bleach signal in the nsTA data and relating this to the number of triplets created. The nsTA data, which uses a 7 ns, 416 nm pump pulse at 0.5 mJ is at a low enough excitation density to eliminate singlet-singlet annihilation. The excitation density was calculated based on the excitation pulse energy (*E*), wavelength (λ), absorption (*A*) at 416 nm, spot size (a), and the film thickness (*l*), using the following equation:

$$\xi = \frac{E \cdot \lambda \cdot K \cdot (1 - 10^{-A})}{l \cdot a} \tag{6}$$

where *K* is a composite of physical constants, $5.034 \cdot 10^{15} \text{ J}^{-1} \text{ nm}^{-1}$.³ Details regarding film thickness are reported on pages S-2 and S-3, and the spot size of pump was matched to probe by using a 0.50 cm diameter aperture. The unit cell volume (V) of the C2/c and Pbcn polymorphs are 1981 Å³ and

1986 Å³, respectively with number of molecules per unit cell (*Z*) equal to 4 for both polymorphs.⁸ Thus, regardless of the polymorph, the number density does not change by more than 0.3 %. Here, the average value between the two, 1983.5 Å³ is used to calculate the number density per unit cell with volume *V*:

$$no.\,density = \frac{z}{v} \tag{7}$$

All the values of parameters used in the above equations are listed in Table S1.

Film	E (mJ/pulse)	λ (nm)	Α	<i>l</i> (nm)	Z (molecules)	$V(Å^3)$
Solvent- annealed	0.5	416	0.18	172	4	1983.5
Thermally annealed	0.5	416	0.18	310	4	1986

Table S1. All of the values used to calculate the scaling factor for ground state depletion method

The ratio ξ / no.density gives a scaling factor for the ground-state absorption spectrum that produces expected bleach at 0 ns delay. We then subtract this expected ground state bleach from the nsTA spectrum at 52 ns to recover the undistorted triplet spectrum with no negative features, which is shown in main text (Inset to Figure 4). Here, 52 ns was chosen to minimize the electronic noise coming from the fluorescence close to time 0. The time-independent triplet yield, φ_T is calculated using the following equation where triplet decay, τ is 80 ± 10 ns (Figure 4):

$$\varphi_T = \varphi_T(t = 52 \, ns) \cdot \frac{1}{e^{-\frac{52 \, ns}{\tau}}} \tag{8}$$

Figure S16 shows the corresponding data for the thermally annealed film. In this case, the data at 40 ns after the nanosecond laser pulse was used to analyze the data, so that

$$\varphi_T = \varphi_T(t = 40 \, ns) \cdot \frac{1}{e^{-\frac{40 \, ns}{\tau}}} \tag{9}$$

Using eq. 6, the calculated excitation density is 4.3×10^{19} excitons/cm³. In terms of excitation density per unit time, a Gaussian 7-ns FWHM pump pulse has 76% of the photons within the integrated FWHM and SF in BPEA occurs with about a 100 ps time constant, so that the effective excitation density over the SF lifetime is $4.3 \times 10^{19} \times 0.76$ / (7000 ps/100 ps) $\approx 4 \times 10^{17}$ excitons/cm³, and thus the singlet-singlet annihilation contribution should be relatively small. Any residual annihilation should makes our yield estimate a lower limit.



Figure S17. (a) The triplet-triplet absorption spectrum determined from the nsTA spectrum at 40 ns using the singlet depletion method.(b) Triplet-triplet absorption decay of the thermally annealed BPEA film ($\tau_1 = 250 \pm 60$ ns (94%); $\tau_2 > 4 \,\mu$ s (6%).

Triplet yield calculation using the spectral deconvolution method.

A detailed description of the Spectral Deconvolution method is given elsewhere.⁹⁻¹⁰ Briefly, the fsTA spectrum can be expressed as a linear combination of species-associated spectrum $\varepsilon_i(\lambda)$, and the time-dependent concentration $c_i(t)$ of species *i*:

$$\Delta A(\lambda, t) = \sum_{i=1}^{n} c_i(t) \cdot \varepsilon_i(\lambda)$$

Thus, knowing the basis spectra ε_i (λ), we can extract populations.⁹⁻¹⁰ Here, we assume there are three independent species contributing to the spectra: ground state bleach, and singlet and triplet

excited state absorptions, (S_0 , S_1 , and T_1 , respectively). The S_0 basis spectrum is obtained from steady-state absorption measurements (**Figure 2**), while S_1 and T_1 spectra are recovered by subtracting the ground-state bleach spectrum from the 1 ps and 300 ps fsTA spectra, respectively (Figure S17).



Figure S18. (a) fsTA spectrum of BPEA thin film with 1 kHz system excited at 414 nm, 0.6 μ J/pulse (b) basis spectra of indicated species to obtain (d) the population dynamics.

This method is performed on three different samples and the values are reported in the **Table S2**, with the average value and standard deviation.

Table S2. Triplet yields of three different samples using the Spectral Devolution method.

	Sample 1	Sample 2	Sample 3	Average
Triplet Yield (%)	154	167	142	150 ± 10

The triplet yield (150 ± 10) % is slightly less than that (180 ± 20) % obtained from the Singlet Depletion method because the analysis is done using high-fluence TA spectra where singlet-singlet annihilation is present. Thus, (150 ± 10) % sets the lower limit for the triplet yield.

Crystal packing structure of C2/c and Pbcn and selected dimer



Figure S19. (a), (c) Crystal packing structure of C2/c polymorph and (b), (d) that of Pbcn.

Figure S20. Selected dimer unit of C2/c polymorph. (a), (c) are dimer 2 and (b), (d) are dimer 3 composed of different neighboring units. Dimer 1 is shown in Figure 1a.

Figure S21. Selected dimer unit of Pbcn polymorph. (a), (c) are dimer 2 and (b), (d) are dimer 3 composed of different neighboring units. Dimer 1 is shown in Figure 1a.

Computational details. The electronic couplings were calculated from the integral matrix elements using the Amsterdam Density Functional (ADF) package¹¹ at the density functional level of theory (DFT). The triple ζ with two polarization functions (TZ2P) basis set and the B3LYP exchange-correlation functional were chosen. Fock and overlap integral matrix elements were calculated using the TRANSFERINTEGRALS key with the fragment orbital approach as implemented in ADF.

The effective coupling between orbitals i and f, V_{if}, was calculated using the following equation:¹²

$$V_{\rm if} = \frac{J_{\rm if} - \frac{1}{2}S_{\rm if}(e_{\rm i} + e_{\rm f})}{1 - S_{\rm if}^2}$$
(10)

where J_{if} is the Fock matrix element between a pair of monomers, S_{if} is the overlap integral, e_i and e_f are the Fock matrix elements within a monomer. The calculated matrix elements are shown in Table S2.

Singlet and triplet excitation energies, $E(S_1)$ and E(T), were calculated using the timedependent density functional theory (TDDFT) with the ADF package. E(TT) was acquired by doubling E(T). The CT state energy, E(CT), was calculated using a Weller-like equation:

$$E(CT) = IP + EA + E_{elec} + E_{ind}$$
(11)

Here, ionization energy (*IP*) and electron affinity (*EA*) of monomer were obtained from DFT, whereas the induction (E_{ind}) and electrostatic (E_{elec}) energies were acquired using the classical Direct Reaction Field (DRF) method¹³ suggested by Mirjani *et al.*¹⁴ Atomic charges of both neutral and charged dimers for DRF calculations were obtained from Mulliken population analysis using DFT. The calculated energies are shown in Table S5.

Table S3. Calculated overlap integrals (S_{if}) , and regular (J_{if}) and effective couplings (V_{if}) between HOMO and LUMO

	Sнн (meV)	SHL (meV)	Slh (meV)	SLL (meV)
Pbcn (dimer 1)	-8.84	5.69	-5.69	1.58
Pbcn (dimer 2)	-4.92	-4.30	4.30	-2.03
Pbcn (dimer 3)	-0.54	0.48	0.41	1.39
C2/c (dimer 1*)	7.05	9.79	-9.79	22.0
C2/c (dimer 2)	-0.65	-0.69	-0.69	2.63
C2/c (dimer 3)	0.02	-0.02	0.02	-0.13
	Jнн (meV)	J _{HL} (meV)	JLH (meV)	J _{LL} (meV)
Pbcn (dimer 1)	109	-66.1	66.1	-15.8
Pbcn (dimer 2)	48.3	41.7	-41.7	18.6
Pbcn (dimer 3)	4.00	-4.66	-4.39	-9.67
C2/c (dimer 1)	-88.1	-111	111	178
C2/c (dimer 2)	6.50	6.25	6.25	-18.9
C2/c (dimer 3)	-0.08	0.08	-0.08	0.71
	V _{HH} (meV)	V _{HL} (meV)	V _{LH} (meV)	VLL (meV)
Pbcn (dimer 1)	61.3	-43.3	43.3	-11.7
Pbcn (dimer 2)	2.14	2.43	-2.43	13.2
Pbcn (dimer 3)	1.04	-2.70	-2.71	-5.94
C2/c (dimer 1)	-50.1	-71.3	71.3	120
C2/c (dimer 2)	2.98	3.46	3.46	-11.8
C2/c (dimer 3)	0.03	0	0	0.36

	J _{SE} (meV)
Pbcn (dimer 1*)	3.73
Pbcn (dimer 2)	1.46
Pbcn (dimer 3)	0.03
C2/c (dimer 1*)	7.81
C2/c (dimer 2)	0.08
C2/c (dimer 3)	0

Table S4. Calculated effective electronic coupling constant for the superexchange model

Table S5. Calculated singlet and triplet excitation, and charge-transfer state energies ($E(S_1)$, E(TT), and E(CT))

	<i>E</i> (S ₁) (eV)	<i>E</i> (TT) (eV)	$E(\mathbf{CT})$ (eV)
Pbcn	2.59	3.00	3.50
C2/c	2.54	2.92	3.51

Table S6. π - π distances, lateral, and longitudinal slip distances in C2/c and Pbcn polymorphs

	Pbcn	C2/c
π-π distance (Å)	3.45	3.40
lateral slip distance (Å)	3.34	4.06
longitudinal slip distance (Å)	0.80	0.80

Molecular Orbital diagrams of Pbcn and C2/c dimers from crystal structures.

Figure S22. (a) and (c) Molecular orbital (MO) diagrams and (b) and (d) the spatial overlap between the two dimers of Pbcn- and C2/c-form BPEA, respectively.

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