

# Supplementary Materials

## for

### Singlet Fission, Polaron Generation and Intersystem Crossing in Hexaphenyl Film

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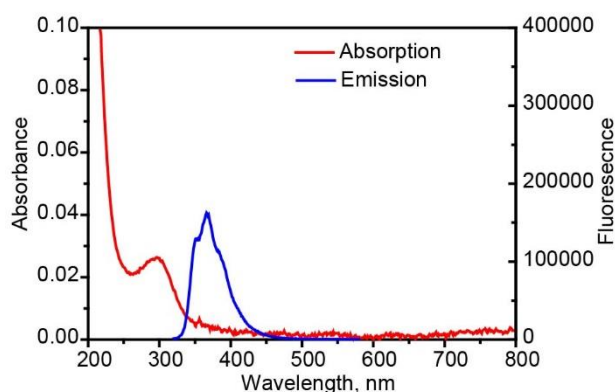
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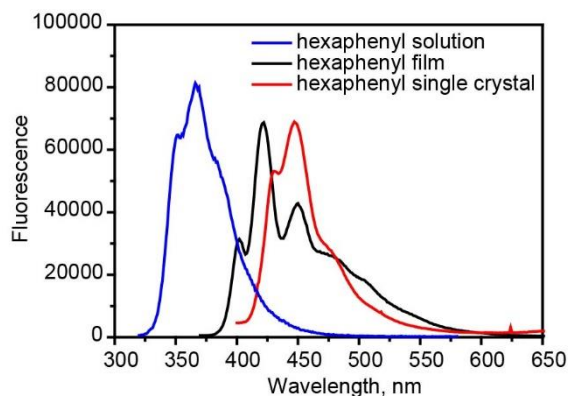
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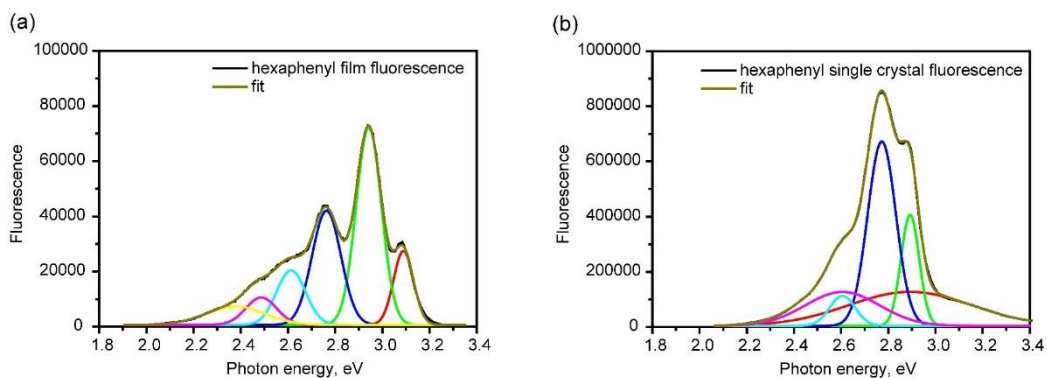
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**Figure S1.** Steady state absorption and fluorescence spectra of hexaphenyl in hexane ( $\lambda_{\text{exc}} = 300$  nm).



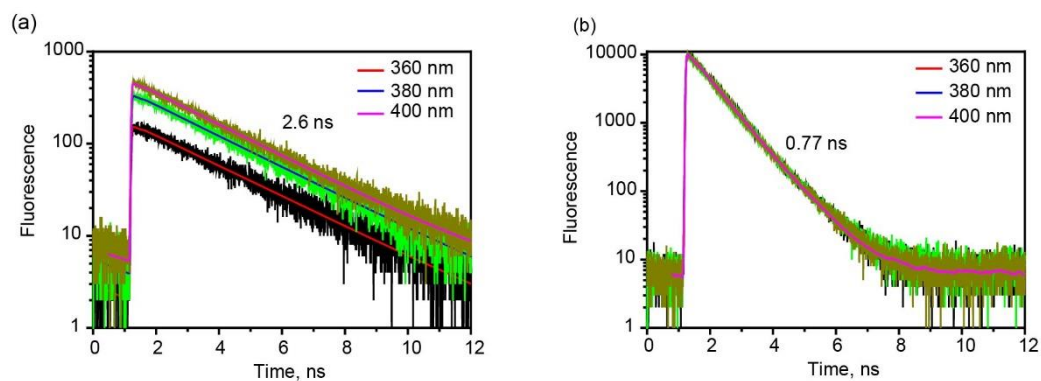
**Figure S2.** Fluorescence of hexaphenyl solution ( $\lambda_{\text{exc}} = 300$  nm), film ( $\lambda_{\text{exc}} = 350$  nm) and single crystal ( $\lambda_{\text{exc}} = 350$  nm).



**Figure S3.** Gaussian fit for steady state fluorescence spectra of (a) hexaphenyl film and (b) single crystal.

**Table S1.** Gaussian multipeak fit maxima of the steady state fluorescence spectra of hexaphenyl film and single crystal.

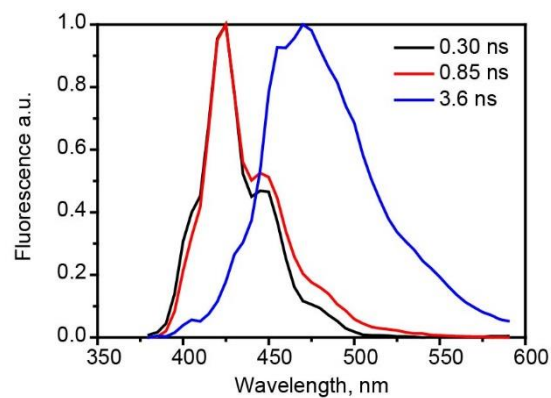
System	Maxima of emission bands [eV]					
Film	2.37	2.49	2.61	2.76	2.94	3.11
Single crystal			2.60	2.77	2.89	



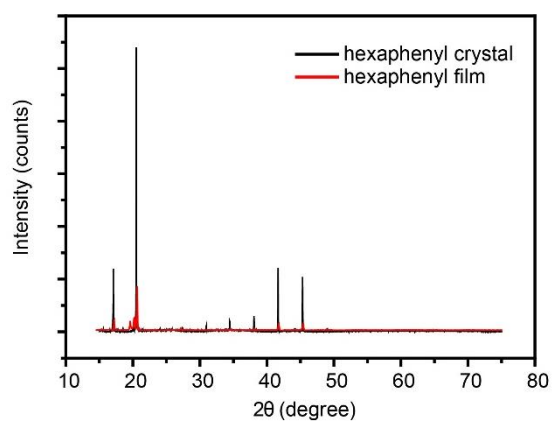
**Figure S4.** Fluorescence decay kinetics of the (a) hexaphenyl crystal and (b) in hexane  $\lambda_{\text{exc}} = 267$  nm at various probe wavelengths.

**Table S2.** Fluorescence decay kinetics of hexaphenyl film, solution and single crystal at various emission wavelengths (TCSPC data).

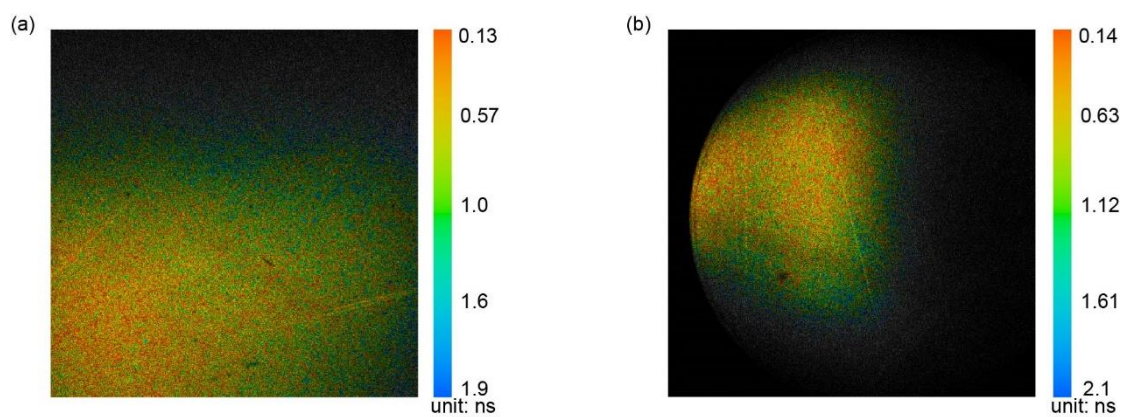
$\lambda_{\text{exc}}$ , nm	$\lambda_{\text{probe}}$ , nm	$\tau_1$ , ns	$A_1$	$\tau_2$ , ns	$A_2$	$\tau_3$ , ns	$A_3$
Film 360	400	0.24	0.62	0.76	0.35	1.6	0.03
	420	0.30	0.70	0.70	0.30	1.9	0.01
	440	0.32	0.67	0.73	0.32	2.9	0.01
	460	0.32	0.60	0.91	0.34	3.9	0.06
	480	0.30	0.57	0.93	0.32	3.4	0.11
	500	0.27	0.44	1.02	0.40	3.4	0.16
	520	0.26	0.42	1.05	0.40	3.5	0.18
Crystal 267	360					2.6	1
	380					2.6	1
	400					2.6	1
Solution 267	360			0.77	1		
	380			0.77	1		
	400			0.77	1		



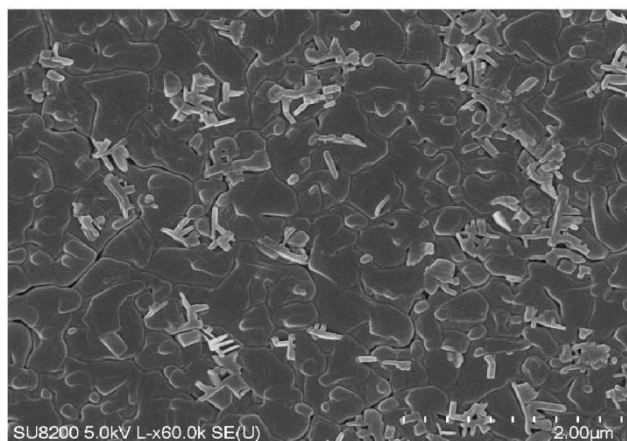
**Figure S5.** Global fit spectra of TCSPC results for hexaphenyl film at  $\lambda_{\text{exc}} = 360$  nm.



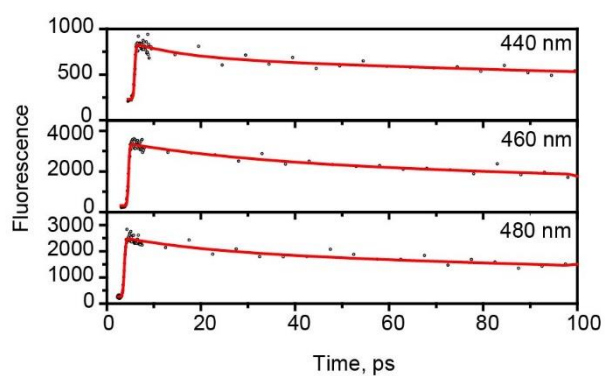
**Figure S6.** X-ray diffraction (XRD) patterns of hexaphenyl film and single crystal presented on the same scale.



**Figure S7.** Fluorescence lifetime imaging acquired with confocal microscopy. Range size (a):  $1 \times 1$   $\mu\text{m}$ , (b):  $10 \times 10$   $\mu\text{m}$ .



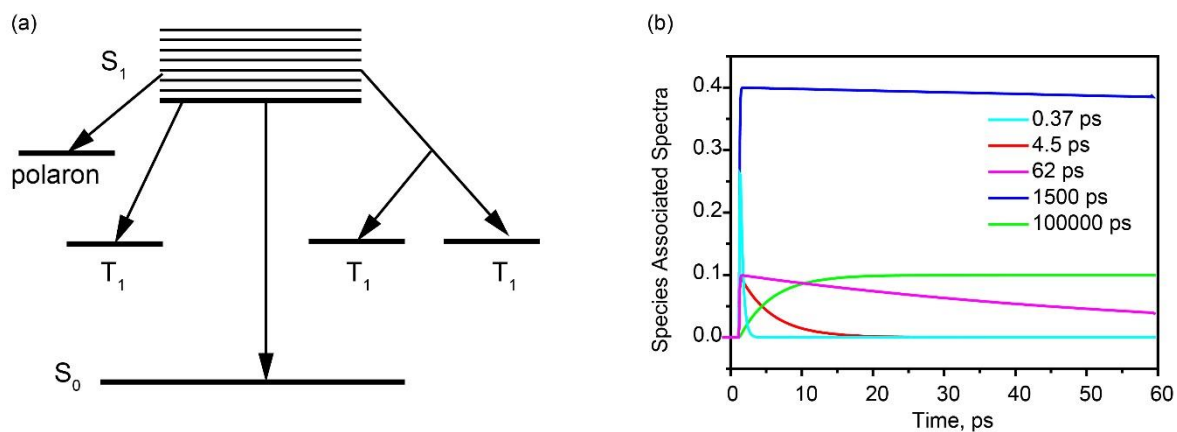
**Figure S8.** Scanning electron microscope (SEM) of hexaphenyl film.



**Figure S9.** Up conversion fluorescence decay kinetics of hexaphenyl film at  $\lambda_{\text{exc}} = 400$  nm.

**Table S3.** Fluorescence decay kinetics of hexaphenyl film at various emission wavelengths (up-conversion data).  $\tau_3$  is fixed to respective TCSPC data.

$\lambda_{\text{exc}}$ , nm	$\lambda_{\text{probe}}$ , nm	$\tau_1$ , ps	$A_1$	$\tau_2$ , ps	$A_2$	$\tau_3$ , ps	$A_3$
400	440	29	0.24	250	0.74	4000 <sup>f</sup>	0.02
	460	35	0.25	300	0.69	4000 <sup>f</sup>	0.06
	490	27	0.22	270	0.70	4000 <sup>f</sup>	0.08



**Figure S10.** Global fit target model (a) and kinetics (b) of Species Associated Spectra.

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Excitation energies and oscillator strengths:

Excited State 1: Singlet-A  3.0022 eV  412.97 nm  f=2.6586 <S**2>=0.000
121->122  0.70148
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1386.01198264
Copying the excited state density for this state as the 1-particle RhoCl density.

Excited State 2: Singlet-A  3.7356 eV  331.90 nm  f=0.0000 <S**2>=0.000
120->122  -0.57289
121->123  -0.39899

Excited State 3: Singlet-A  3.9383 eV  314.81 nm  f=0.0000 <S**2>=0.000
120->122  0.40184
121->123  -0.57400
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**Figure S11.** TD-DFT/(b3lyp/6-31g(d)) calculation of excited singlet state energies of hexaphenyl isolated molecule at  $S_1$  geometry.

Excitation energies and oscillator strengths:

Excited State 1: 3.007-A 0.1408 eV 8803.98 nm f=0.0001 <S\*\*2>=2.011

122A ->123A	0.92075
122A ->131A	0.29118
110B ->121B	0.10256
112B ->121B	-0.30610
120B ->121B	0.95325
122A <-123A	0.64240
122A <-131A	0.24087
112B <-121B	-0.24646
120B <-121B	0.64186

This state for optimization and/or second-order correction.  
Total Energy, E(TD-HF/TD-KS) = -1387.41406581  
Copying the excited state density for this state as the 1-particle RhoCI density.

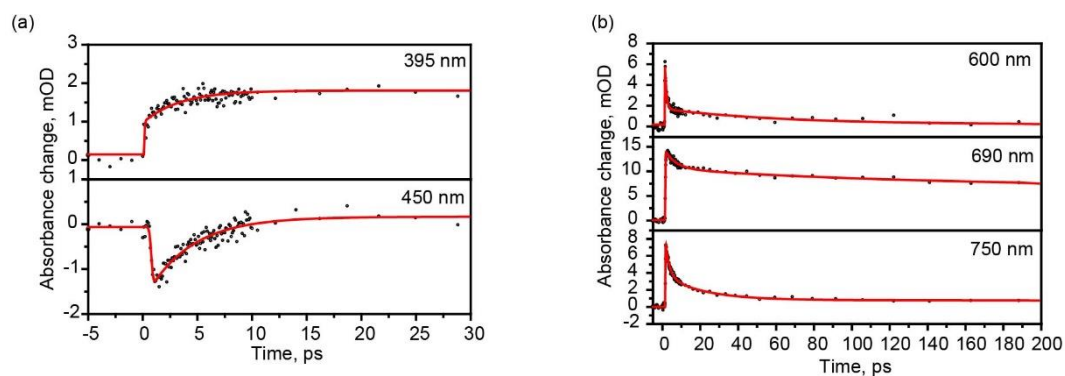
Excited State 2: 3.027-A 1.0392 eV 1193.05 nm f=0.0000 <S\*\*2>=2.041

122A ->125A	0.75914
122A ->126A	-0.17439
122A ->127A	-0.23375
122A ->128A	-0.11946
114B ->121B	0.10107
118B ->121B	0.54314

Excited State 3: 3.013-A 1.0921 eV 1135.25 nm f=0.0007 <S\*\*2>=2.020

122A ->124A	-0.64054
122A ->132A	-0.11947
111B ->121B	0.13653
119B ->121B	0.74909

**Figure S12.** TD-DFT/(b3lyp/6-31g(d)) calculation of excited triplet state energies of hexaphenyl isolated molecule at T<sub>1</sub> geometry.



**Figure S13.** Decay kinetics of the hexaphenyl film  $\lambda_{\text{exc}} = 250$  nm at different wavelengths.

**Table S4.** Lifetimes obtained from fit/deconvolution of TA spectra for the hexaphenyl film at  $\lambda_{\text{exc}} = 250$  nm; f = fixed.

$\lambda_{\text{exc}}$ , nm	$\lambda_{\text{probe}}$ , nm	$\tau_1$ , ps	$A_1$	$\tau_2$ , ps	$A_2$	$\tau_3$ , ps	$A_3$	$\tau_4$ , ps	$A_4$
250	395	3.4	-0.47					$100000^f$	1
	450	4.1	-0.74			3300	-0.26	$100000^f$	1
	600	0.80	0.76	63	0.24				
	690	5.9	0.25	100	0.19	1600	0.39	$100000^f$	0.17
	750	2.1	0.55	21	0.37	2900	0.08		