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Femtosecond Stimulated Raman Spectroscopy - Guided Library Mining Leads to Efficient

Singlet Fission in Rubrene Derivatives

Supporting Information

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Experimental Details:

Sample preparation. We grew crystalline rubrene via a physical vapor deposition (PVT) method.¹ Briefly, we used 16 mg of rubrene powder, \geq 98% purity from Sigma Aldrich in the PVT furnace with Ar gas flowing at the rate of 100 ml/min. We heated the source region in the furnace to 330°C using a thermocouple for 35 minutes and obtained 4-6 mm long needle-shaped orange colored rubrene crystals at a distance of 5-8 cm away from the source region.

We obtained the raw material of FM-rubrene and F-rubrene powder from McGarry et al.² to grow their single crystals via slow solvent evaporation method. We dissolved the raw powder in a minimum amount of CH₂Cl₂ and layered the top of the solution with isopropanol in the ratio of 1:4 CH₂Cl₂:isopropanol and left it standing at room temperature under nitrogen gas environment until crystals had formed. We obtained 2-3 mm long and wide, plate-shaped, red-colored FM-rubrene and F-rubrene crystals. We separately mounted each of the crystals used in this work onto a 1 mm thick glass microscope slide and sealed them with a glass coverslip and glue.

UV-Vis spectroscopy. We obtained the absorption spectra of rubrene, FM-rubrene and F-rubrene crystals using UV2600 UV-Vis spectrophotometer by Shimadzu in transmission mode. We plot the normalized steady-state absorption spectra of crystalline rubrene, FM-rubrene and F-rubrene along with the respective crystal image as seen under the microscope for our FSRS studies in Figure S1. The absorption spectrum of a rubrene single crystal shows four absorbance maximum at 438, 464, 497 and 536 nm, FM-rubrene single crystal shows the absorbance maxima at 442, 468, 500 and 560 nm and F-rubrene crystal peaks at 466, 510, 531 and 557 nm. The poor resolution of the peaks in F-rubrene crystal is due to the smaller crystallite size. The estimated crystal thickness of rubrene is \sim 1-2 µm, FM-rubrene and F-rubrene are \sim 30-40 µm.



Figure S1. Molecular structure and the respective crystals of rubrene, FM-rubrene and F-rubrene along with their absorption spectrum. Scale bar is 0.2 mm.

Continuous wave Raman spectra. We obtained the spontaneous Raman spectra of rubrene, FMrubrene and F-rubrene crystals using a home-built Raman spectrometer. We sent a 785 nm laser through an inverted Olympus IX 73 microscope and focused it onto the samples through a 10x Olympus objective. The power of the laser at the sample was 90 mW and we collected the Raman signal in a transmission geometry using a Princeton Instruments 2500i spectrograph and a Princeton Instruments PIXIS 100BX CCD array.

Femtosecond stimulated Raman spectroscopy. We measured time-resolved FSRS experiments on our home-built optical setup, described elsewhere.^{1,3–6} Briefly, we used the fundamental output

of 4.6 W at 800 nm from a 1 kHz repetition rate Ti:Sapphire regenerative amplifier (Coherent model Libra-F-1K-HE-110) to generate the Raman pump, Raman probe and actinic pulses for the FSRS experiments.

We used two different setups to generate Raman pump pulses for the experiments presented in this article. We used a custom grating filter to generate the Raman pump pulse by sending 480 mW of the fundamental output through the grating filter to generate a 2.1 ps Raman pump pulse for rubrene FSRS data. We also passed 450 mW of the fundamental output through a custom etalon (TecOptics) to produce a 4 ps narrowband Raman pump pulse centered at 807 nm for FM-rubrene and F-rubrene FSRS studies. We then passed these pulses through an optical chopper synced with the laser repetition rate to block every other Raman pump pulse.

We focused 2.5 mW of the 800 nm fundamental output through a 2 mm sapphire crystal to generate a white light continuum as the Raman probe. We passed the continuum through an 830 nm long-pass filter to block the residual 800 nm output. We then compressed the pulses with a fused silica prism pair to generate the femtosecond broadband Raman probe. We set the path length of the Raman pump pulse and Raman probe pulse to be the same and overlapped them temporally for the FSR measurements.

We used a home-built non-collinear optical parametric amplification (NOPA) system to generate the actinic pulse. We generated the white light seed continuum in a 2 mm thick sapphire crystal and used a BBO crystal to generate the 400 nm pulse by frequency doubling the 800 nm fundamental output. In our NOPA set-up, we mixed the white light continuum and the doubled fundamental pump pulse in a 1 mm BBO mixing crystal. We then passed the generated visible pulse through a newly installed pulse shaper (Fastlite DazzlerTM) and an SF10 prism pair compressor for compression and dispersion compensation to generate the actinic pulse. To collect

time-resolved data, we used an actinic pulse with a central wavelength of 536 nm and full-width half maximum of 14 nm for crystalline rubrene and a 533 nm actinic pulse with 10 nm full-width half maximum for crystalline FM-rubrene and F-rubrene, shown in Figure S2. We performed the time-resolved experiments on different days with different alignments, which resulted in slightly different actinic pulse central wavelength.

We sent all the three pulses to the sample through an inverted Olympus IX 73 microscope and focused the Raman pump, Raman probe and actinic pump pulse collinearly onto the sample using a 6 cm focal length lens and used a condenser (Olympus IX2-LWUCD, NA 0.55) to collimate the Raman probe pulse to the detector. We controlled the time delay between the actinic pulse and the Raman probe pulse using a piezoelectric delay stage (Thorlabs, DDS220). We measured the cross-correlation of the actinic pump and Raman probe pulses to be 120 ± 2 fs with 533 nm actinic pump pulse for FM-rubrene and F-rubrene studies and 250 ± 2 fs with 536 nm actinic pump pulse for rubrene FSR measurements by the optical Kerr effect with a 2 mm cuvette of cyclohexane. The better cross-correlation for the FM-rubrene and F-rubrene measurements is attributed to better compression of the actinic pulse by the newly mounted pulse shaper (Dazzler), which was absent for the rubrene studies. For all measurements, we used a 10 cm lens to focus the stimulated Raman signal and the probe onto a 1/3 meter spectrograph and a Princeton Instruments PIXIS 100F CCD array to collect the Raman spectra with an acquisition rate of 1 kHz. We used a customized LabVIEW program to obtain the femtosecond stimulated Raman gain spectra by collecting the ratio of the Raman probe spectra with the Raman pump on and the Raman pump off.

Actinic pulse profile:

We tuned the actinic pump pulse to have a central frequency of 536 nm to collect FSR data for rubrene and 533 nm for FM-rubrene and F-rubrene crystals and plot the spectral profile in Figure S2.



Figure S2. Spectral profile of the actinic pump pulses used to carry out the FSR experiments. We used the 533 nm as the central frequency of the actinic pump pulse with a FWHM of 10 nm to collect time-resolved data in FM-rubrene and F-rubrene crystals, and 536 nm with a FWHM of 14 nm for crystalline rubrene.

Raw FSR data of crystalline rubrene, FM-rubrene and F-rubrene:

We plot the FSR data after one-to-one subtraction of excited state spectra from the ground state spectrum of crystalline rubrene, FM-rubrene and F-rubrene in Figure S3. We used a grating filter to generate the Raman pump pulse for the FSR experiments in crystalline rubrene¹ and an etalon to generate the Raman pump pulse for FM-rubrene and F-rubrene FSR experiments. The ground state Raman spectra of rubrene, FM-rubrene and F-rubrene has peaks at 1204, 1304, 1430 and 1541 cm⁻¹. After photoexcitation, we observe ground state bleaching features for all the Raman modes due to decreased population of the ground singlet state, S₀.



Figure S3. Raw FSR data of crystalline (**a**) rubrene (**b**) FM-rubrene and (**c**) F-rubrene at various time delays after photoexcitation. The dashed lines represent the ground state Raman modes in the three molecules.

Kinetics of ground state addition:

The large depletion of the ground state peaks in the excited state spectra after photoexcitation necessitated the addition of ground state spectra to examine the dynamics in the excited states. We added a fraction of ground state back into the excited state spectra until no bleaching features at ground state frequencies remained. We experimented with multiple ground state Raman features for the ground state addition, such as 1304 cm⁻¹ and 1541 cm⁻¹ individually, and they all resulted into similar dynamics irrespective of the feature used to add back the ground state. We present the spectra obtained after adding back the ground state to the excited state spectra for the three rubrene analogues in Figure 2 of the main text. We plot the kinetics of the percentage of the ground state added back to excited state spectra in Figure S4 which is the same as the kinetics of the ground state depletion.



Figure S4. Time resolved kinetics of percentage of ground state spectra added to excited state spectra at different time delays with corresponding exponential fits for rubrene, FM-rubrene and F-rubrene FSR data.

FSR data of crystalline FM-rubrene with a grating filter:

We used a grating filter setup to collect the FSR data of rubrene and an etalon for the FSR data of FM-rubrene and F-rubrene presented in Figure 2 of main text. To validate that the dynamics after photoexcitation remains unchanged irrespective of the Raman pump generation method, we obtained time-resolved FSR data of FM-rubrene using a grating filter. We present the raw FSR data of FM-rubrene using the grating filter in Figure S5a and the FSR spectra obtained after adding

partial ground state spectra to the excited state spectra in Figure S5b. We present the kinetics of the amount of ground state spectra added back to excited state spectra which is nothing but the dynamics of the ground state depletion in Figure S6. As a proof, the dynamics remain unchanged between using a grating filter and an etalon to generate the Raman pump pulses.



Figure S5. (a) Raw FSR data of FM-rubrene collected with Raman pump pulses generated with a grating filter as the Raman pump source. (b) Corresponding FSR data after adding back fraction of ground state spectrum to the excited state spectra to remove any ground state bleaching features. The shaded region indicates the excited state Raman feature (blue).



Figure S6. Time resolved kinetics of percentage of ground state spectra added to excited state spectra at different time delays with exponential fit for FM-rubrene (blue) FSR data collected with Raman pump generated using a grating filter.

To further confirm that the spectral evolution of the 1430 cm⁻¹ mode remains unchanged between using an etalon and a grating filter to generate Raman pump pulses, we plot the dynamics of the Raman frequency shift of the 1430 cm⁻¹ mode from Figure S5b with its corresponding exponential fit in Figure S7. The exponential fit gives a time constant of 140 ± 30 fs for the frequency shift of the 1430 cm⁻¹ mode here using the grating filter, which is in agreement with the time constant of 150 ± 20 fs obtained with an etalon in the main text.



Figure S7. Transient evolution of the Raman mode around 1430 cm⁻¹ in FM-rubrene using a grating filter as the Raman pump pulse generation source.

Transient absorption in crystalline rubrene, FM-rubrene and F-rubrene:

We plot the transient absorption (TA) spectra, which is in the presence of only the actinic pulse and Raman probe pulse, of rubrene, FM-rubrene and F-rubrene in Figure S8. We observe strong intense positive features below 900 nm in all three molecules, which is indicative of excited state absorption. These features are very long-lived, on the order of the lifetimes of triplet states. The broad features below 1200 cm⁻¹ in our FSRS data match those intense features here from the transient absorption by the excited state species.



Figure S8. Transient absorption data in crystalline (**a**) rubrene (**b**) FM-rubrene and (**c**) F-rubrene. The intense positive peaks below 900 nm indicate the presence of excited state absorption features.

Transient absorption of FM-rubrene solution in chloroform:

In order to verify the assignment of the TA features observed in crystalline FM-rubrene, we collected the TA data of solution FM-rubrene. We plot the TA spectra of FM-rubrene in chloroform and crystal form in Figure S9a and S9b respectively. Comparing the TA of FM-rubrene in solution and crystal, we notice that the strong long-lived peaks at around 875 nm and 892 nm in crystal are absent in the solution data. This confirms that the strong positive peaks present in the TA data of crystalline FM-rubrene is due to absorption by the excited states which are not accessible in solution FM-rubrene, and the peaks correspond to the long-lived triplet states formed through singlet fission. The absence of positive features in solution TA data and the long lifetime of the intense positive features in crystalline FM-rubrene is a strong evidence for FM-rubrene to undergo singlet fission in crystal form, similar to that observed in rubrene.⁷



Figure S9. Transient absorption spectra of (a) FM-rubrene solution in chloroform and (b) crystal. The absence of the intense positive features in the FM-rubrene solution data indicates that there is no absorption from excited states which are in resonance with our probing system.

Time-resolved kinetic fit of 1430 cm⁻¹ at time zero in crystalline rubrene:

We fit the frequency evolution of the 1430 cm⁻¹ Raman mode in crystalline rubrene with two exponentials and three exponential functions. As mentioned in the main text, in both the scenario, a time constant of tens of nanoseconds, corresponding to the triplet lifetime, was held constant to fit the amplitude dynamics of the Raman mode. We show the fits with biexponential and triexponential fit function over various time delays in Figure S10. We tabulate the associated time constants and their errors in Table S1 below.



Figure S10. Time-resolved kinetics of Raman frequency shifts of the mode around 1430 cm⁻¹ at time zero in crystalline rubrene. Markers in red are the Raman mode frequencies at various time delays in crystalline rubrene, blue colored fit corresponds to biexponential fit, and yellow color corresponds to fit with three exponentials.

Table S1. Time constants obtained from exponential fits of the Raman frequencies of crystalline

 rubrene from Figure R1.

	$ au_1$	$ au_2$	$ au_3$ (constant)
Biexponential Fit		$3.3 \pm 0.2 \text{ ps}$	10 ns
Triexponential Fit	$231 \pm 274 \text{ fs}$	$3.5 \pm 0.3 \text{ ps}$	10 ns

From Figure S10 and Table S1, we observe that the biexponential fit of the frequency shifts renders a time constant of 3.3 ± 0.2 ps. Whereas adding an additional shorter time constant to the fit, as in the triexponential function, gives a fast time of 231 ± 274 fs and a slower time duration of 3.5 ± 0.3 ps. However, the error associated with the fit of the fast time constant of 231 ± 274 fs is large, suggesting a poor fit. Also, the obtained fast time constant is comparable to the instrument response function in out experiments, 250 ± 2 fs. Additionally, the fit of the frequency shift does not improve upon adding an additional time constant, and thus we have considered using two time constants to extract the kinetics of the evolution of the 1430 cm⁻¹ Raman mode.

Kinetic fit of the broad features in rubrene, FM-rubrene and F-rubrene:

The broad features below 1200 cm⁻¹ in FSRS data in Figure 2 are electronic features from the transient absorption by the separated triplet states. We fit the amplitude of the broad features to a Gaussian wavefunction and fit the amplitudes to a biexponential function to obtain the kinetics in Figure S11. The broad features below the 1200 cm⁻¹ region grows in on a timescale of 9.9 ± 0.8 ps in rubrene, $4.9 \text{ ps} \pm 0.4 \text{ ps}$ in FM-rubrene and $4.6 \pm 0.4 \text{ ps}$ in F-rubrene. A second time constant of tens of nanoseconds, corresponding to the triplet lifetime, was held constant to fit the amplitude dynamics of these features. These transient absorption signatures of the separated triplet states demonstrate that the separated triplets are formed faster in F-rubrene, followed by FM-rubrene and rubrene. The frequency evolution of the Raman vibrational mode in the main text relates to the structural evolution dynamics during the triplet pair separation ¹(T...T), whereas the transient absorption signatures, which arise on the longer timescales, are that of the separated triplet states in the rubrene and the derivatives during singlet fission. Differences between time constants observed in transient absorption microscopy and FSRS have been observed in all previously published singlet fission studies involving FSRS, and thus we emphasize the relative comparison between the FSRS results here rather than the absolute numbers.



Figure S11. Amplitude kinetics of the broad features below 1200 cm⁻¹ in rubrene, FM-rubrene and F-rubrene FSRS data arising from transient absorption of the excited states.

Kinetic fits of experimental frequency shifts in FM-rubrene:

The time constants (τ_1) associated with the kinetic fits for FM-rubrene and F-rubrene in Figure 3a is 150 ± 20 fs and less than 120 ± 40 fs, respectively. Given our instrument response function is 120 ± 3 fs, the kinetic fits are approaching the instrument response function and thus

the errors in the time constants become significant. To demonstrate the sensitivity of the overall fit for the completion of the frequency shift on the time constant, we present five fits with varying time constants (110, 130, 150, 170 and 190 fs) to model the dynamic frequency evolution of the 1430 cm⁻¹ mode in FM-rubrene in Figure S12. We observe the problem associated with the fit while using time constants that are outside the uncertainty of the fit presented in the main text. It is not possible to accurately model the early growth dynamics of the Raman mode around 1430 cm⁻¹ with time constants that are either shorter or longer than the uncertainty window in 150 ± 20 fs. This demonstrates that the errors associated with the time constants are significant and reliable. The time constants obtained with F-rubrene is much faster than the instrument response function of our experiments, and we have thus considered the instrument response function as the upper bound for the time constant in F-rubrene as mentioned in the main text.



Figure S12. Best possible fits with time constants 110, 130, 150, 170 and 190 fs for the transient frequency shift of the 1430 cm^{-1} mode.

Franck-Condon activity similarity:

To ascertain that the Franck Condon (FC) activity is similar in the three compounds, we measured the absorption spectral profiles of rubrene, FM-rubrene and F-rubrene in solution and plot them in Figure S13. We obtained the absorbance at 525 nm to be 0.74, 0.62 and 0.69 in 0.37 mM rubrene, 0.39 mM FM-rubrene and 0.36 mM F-rubrene solutions. This indicates that their FC

activities are similar within 17% of each other when the concentrations are within 8% range. Given the extremely small quantities of sample available necessitating some degree of uncertainty in the concentration, we conclude that there is no evidence for difference in FC activity.



Figure S13. Absorption spectral profiles of rubrene, FM-rubrene and F-rubrene in solution with their associated concentrations.

Coordinates of optimized geometries from DFT Calculations:

We optimized the geometries of rubrene, FM-rubrene and F-rubrene in their ground singlet state and triplet electronic states, starting with geometry coordinates from their crystallographic data. All the optimized geometries have a planar backbone, and the associated coordinates are present in Tables S1-S6.

Table S2: Optimized geometry of ground singlet state in rubrene.

Atom	Х	Y	Ζ
С	0	0	0.737135
С	1.248596	0.098236	1.429003
С	2.437921	0.364478	0.723047
С	3.694226	0.556431	1.398336

С	4.855175	0.769838	0.711778
С	1.410622	-0.269273	2.876813
С	1.615924	0.680275	3.88743
С	1.876741	0.281756	5.198128
С	1.949412	-1.074651	5.520579
С	1.760205	-2.029767	4.521335
С	1.49767	-1.629177	3.211219
Н	3.709858	0.541518	2.479877
Н	5.783512	0.929797	1.252401
Н	1.560243	1.736381	3.64388
Н	2.024002	1.033275	5.968448
Н	2.15603	-1.383394	6.541233
Н	1.824851	-3.088087	4.758519
Н	1.364043	-2.374625	2.432487
С	-1.248596	-0.098236	1.429003
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Н	1.824851	-3.088087	-4.758519
Н	1.364043	-2.374625	-2.432487

 Table S3: Optimized geometry of triplet state in rubrene.

Atom	Х	Y	Z
С	0	0	0.738459
С	1.244761	0.066943	1.425607
С	2.471071	0.375148	0.714717
С	3.687255	0.613214	1.387757
С	4.866003	0.881448	0.697191
С	1.396723	-0.359916	2.852417
С	1.690702	0.52955	3.897065
С	1.918725	0.061712	5.190609
С	1.871568	-1.306682	5.463386
С	1.591125	-2.203587	4.432156
С	1.357539	-1.733859	3.139797
Н	3.708621	0.579944	2.469239
Н	5.781572	1.071442	1.249403
Н	1.720017	1.59556	3.695564

Н	2.13192	0.768724	5.987223
Н	2.053648	-1.669753	6.470726
Н	1.559138	-3.271254	4.630992
Н	1.148134	-2.434923	2.33713
C	-1.244761	-0.066943	1.425607
С	-2.471071	-0.375148	0.714717
C	-3.687255	-0.613214	1.387757
C	-4.866003	-0.881448	0.697191
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Н	2.13192	0.768724	-5.987223
Н	2.053648	-1.669753	-6.470726
Н	1.559138	-3.271254	-4.630992
Н	1.148134	-2.434923	-2.33713

Table S4: Optimized geometry of ground singlet state in FM-rubrene.

Atom	Х	Y	Ζ
С	-0.94799	0.358734	1.426421
С	-2.11578	0.706277	0.72233
С	-3.35195	1.002427	1.398262
Н	-3.3697	0.996046	2.479785
С	-4.49301	1.304018	0.711839
Н	-5.40519	1.538515	1.252402
С	5.066004	-1.02436	0.711965
Н	5.978063	-1.26085	1.252089
С	3.926224	-0.71918	1.399113
Н	3.940563	-0.71032	2.48071
С	2.691534	-0.42075	0.722107
С	1.526428	-0.07073	1.430026
С	0.290195	0.143544	0.738412
С	-1.14042	0.081223	2.890561
С	-1.17709	1.103594	3.849416
Н	-0.98464	2.126516	3.544696
С	-1.43246	0.818803	5.186432
Н	-1.44261	1.616599	5.921318
С	-1.67369	-0.49863	5.586488
С	-1.6871	-1.52202	4.63768
Н	-1.89784	-2.54068	4.944431
С	-1.43067	-1.22838	3.300162
Н	-1.44671	-2.02404	2.561683
С	1.713991	0.203419	2.894847
С	1.998803	1.508582	3.315606
Н	2.01819	2.311051	2.583414

С	2.249604	1.791093	4.659515
Н	2.456326	2.815334	4.960436
С	2.23306	0.780186	5.626025
С	1.986714	-0.53196	5.195661
Н	1.968931	-1.33747	5.925392
С	1.74215	-0.81752	3.85606
Н	1.550122	-1.84134	3.55041
С	-1.82997	-0.80747	7.046969
F	-2.50943	0.160895	7.701932
F	-0.62136	-0.91251	7.664398
F	-2.47591	-1.97404	7.260695
С	2.451602	1.073923	7.090707
Н	3.334389	0.552314	7.478337
Н	1.593096	0.736693	7.682292
Н	2.590213	2.143526	7.270439
С	-0.94799	0.358734	-1.42642
С	-2.11578	0.706277	-0.72233
С	-3.35195	1.002427	-1.39826
Н	-3.3697	0.996046	-2.47979
С	-4.49301	1.304018	-0.71184
Н	-5.40519	1.538515	-1.2524
C	5.066004	-1.02436	-0.71197
Н	5.978063	-1.26085	-1.25209
С	3.926224	-0.71918	-1.39911
Н	3.940563	-0.71032	-2.48071
С	2.691534	-0.42075	-0.72211
С	1.526428	-0.07073	-1.43003
С	0.290195	0.143544	-0.73841
С	-1.14042	0.081223	-2.89056
С	-1.17709	1.103594	-3.84942
Н	-0.98464	2.126516	-3.5447
С	-1.43246	0.818803	-5.18643
Н	-1.44261	1.616599	-5.92132
С	-1.67369	-0.49863	-5.58649
С	-1.6871	-1.52202	-4.63768
Н	-1.89784	-2.54068	-4.94443
С	-1.43067	-1.22838	-3.30016
Н	-1.44671	-2.02404	-2.56168
С	1.713991	0.203419	-2.89485
С	1.998803	1.508582	-3.31561
Н	2.01819	2.311051	-2.58341
C	2.249604	1.791093	-4.65952
Н	2.456326	2.815334	-4.96044
С	2.23306	0.780186	-5.62603

C	1.986714	-0.53196	-5.19566
Н	1.968931	-1.33747	-5.92539
С	1.74215	-0.81752	-3.85606
Н	1.550122	-1.84134	-3.55041
С	-1.82997	-0.80747	-7.04697
F	-2.50943	0.160895	-7.70193
F	-0.62136	-0.91251	-7.6644
F	-2.47591	-1.97404	-7.2607
С	2.451602	1.073923	-7.09071
Н	3.334389	0.552314	-7.47834
Н	1.593096	0.736693	-7.68229
Н	2.590213	2.143526	-7.27044

Table S5: Optimized geometry of triplet state in FM-rubrene.

Atom	Х	Y	Ζ
С	0.954896	0.377863	-1.42416
С	2.151639	0.78215	-0.71393
С	3.341206	1.129702	-1.38756
Н	3.364546	1.108842	-2.46928
С	4.493706	1.495937	-0.69697
Н	5.388694	1.765857	-1.24931
С	-5.03263	-1.20061	-0.69716
Н	-5.92505	-1.48019	-1.24899
С	-3.88501	-0.82059	-1.38843
Н	-3.90602	-0.79576	-2.47016
С	-2.69944	-0.46304	-0.71357
С	-1.50873	-0.04546	-1.42646
С	-0.27706	0.16623	-0.74105
С	1.152064	0.061333	-2.875
С	1.24499	1.058412	-3.8581
Н	1.102773	2.096617	-3.57837
С	1.482006	0.72996	-5.18802
Н	1.530928	1.50892	-5.94146
С	1.650139	-0.60754	-5.5582
С	1.60992	-1.60814	-4.58648
Н	1.762232	-2.64365	-4.8705
С	1.370538	-1.27119	-3.25573
Н	1.339799	-2.05019	-2.50022
C	-1.70412	0.273078	-2.87625
C	-1.91694	1.603419	-3.26131
Н	-1.88408	2.386245	-2.50876

C	-2.16014	1.934539	-4.59551
Н	-2.31099	2.976383	-4.86783
C	-2.20189	0.950856	-5.58891
C	-2.02371	-0.3838	-5.19578
Н	-2.04578	-1.16834	-5.94786
С	-1.79208	-0.71862	-3.86567
Н	-1.64786	-1.75883	-3.59066
С	1.780793	-0.95441	-7.01262
F	2.537741	-0.05661	-7.68337
F	0.567399	-0.96864	-7.62911
F	2.328339	-2.17355	-7.20548
С	-2.41043	1.294773	-7.04406
Н	-3.3362	0.854654	-7.43277
Н	-1.5878	0.903604	-7.65328
Н	-2.46484	2.375843	-7.19859
С	0.954896	0.377863	1.424163
С	2.151639	0.78215	0.713927
С	3.341206	1.129702	1.387558
Н	3.364546	1.108842	2.469278
С	4.493706	1.495937	0.696967
Н	5.388694	1.765857	1.249306
С	-5.03263	-1.20061	0.697158
Н	-5.92505	-1.48019	1.248988
С	-3.88501	-0.82059	1.38843
Н	-3.90602	-0.79576	2.470157
С	-2.69944	-0.46304	0.71357
С	-1.50873	-0.04546	1.426458
С	-0.27706	0.16623	0.741053
С	1.152064	0.061333	2.874996
С	1.24499	1.058412	3.8581
Н	1.102773	2.096617	3.578368
С	1.482006	0.72996	5.188018
Н	1.530928	1.50892	5.941462
С	1.650139	-0.60754	5.558204
С	1.60992	-1.60814	4.586483
Н	1.762232	-2.64365	4.870495
С	1.370538	-1.27119	3.255729
Н	1.339799	-2.05019	2.500217
С	-1.70412	0.273078	2.876252
С	-1.91694	1.603419	3.26131
Н	-1.88408	2.386245	2.508756
С	-2.16014	1.934539	4.59551
Н	-2.31099	2.976383	4.867828
С	-2.20189	0.950856	5.588912

С	-2.02371	-0.3838	5.19578
Н	-2.04578	-1.16834	5.947863
С	-1.79208	-0.71862	3.865673
Н	-1.64786	-1.75883	3.590663
С	1.780793	-0.95441	7.012615
F	2.537741	-0.05661	7.683371
F	0.567399	-0.96864	7.629106
F	2.328339	-2.17355	7.205483
С	-2.41043	1.294773	7.044058
Н	-3.3362	0.854654	7.43277
Н	-1.5878	0.903604	7.653277
Н	-2.46484	2.375843	7.198591

Table S6: Optimized geometry of ground singlet state in F-rubrene.

Atom	Х	Y	Ζ
С	0.83432	0.494886	1.42559
С	1.989528	0.886198	0.723011
С	3.21778	1.210927	1.398634
Н	3.236262	1.199494	2.480294
С	4.349583	1.54556	0.711856
Н	5.255585	1.803483	1.252099
С	-5.13632	-1.04173	0.711832
Н	-6.04107	-1.30448	1.252011
С	-4.00659	-0.70061	1.398996
Н	-4.02302	-0.68805	2.48061
С	-2.78028	-0.37	0.722986
С	-1.62834	0.026451	1.429436
С	-0.39809	0.260512	0.736853
С	1.028905	0.147891	2.873343
С	1.256875	-1.19512	3.210172
Н	1.229846	-1.94937	2.429807
С	1.512447	-1.57128	4.52587
Н	1.684206	-2.61317	4.774128
С	1.55536	-0.6009	5.52887
С	1.363518	0.744436	5.204487
Н	1.410451	1.498618	5.982261
С	1.111748	1.113336	3.886187
Н	0.956568	2.15844	3.641046
С	-1.82739	0.374018	2.877808
С	-1.90642	-0.59036	3.892443
Н	-1.73498	-1.63403	3.648935

С	-2.18108	-0.22056	5.209064
Н	-2.20903	-0.97841	5.986239
С	-2.40522	1.119692	5.530346
Н	-2.6217	1.405883	6.555336
С	-2.35269	2.086649	4.525784
Н	-2.53782	3.130597	4.762914
С	-2.06765	1.715758	3.21153
Н	-2.03479	2.469496	2.429997
С	1.726257	-1.01088	6.963636
F	2.466137	-2.13574	7.08662
F	2.32457	-0.04821	7.700548
F	0.530614	-1.2658	7.553697
С	0.83432	0.494886	-1.42559
С	1.989528	0.886198	-0.72301
С	3.21778	1.210927	-1.39863
Н	3.236262	1.199494	-2.48029
С	4.349583	1.54556	-0.71186
Н	5.255585	1.803483	-1.2521
C	-5.13632	-1.04173	-0.71183
Н	-6.04107	-1.30448	-1.25201
С	-4.00659	-0.70061	-1.399
Н	-4.02302	-0.68805	-2.48061
C	-2.78028	-0.37	-0.72299
C	-1.62834	0.026451	-1.42944
C	-0.39809	0.260512	-0.73685
C	1.028905	0.147891	-2.87334
С	1.256875	-1.19512	-3.21017
Н	1.229846	-1.94937	-2.42981
С	1.512447	-1.57128	-4.52587
Н	1.684206	-2.61317	-4.77413
С	1.55536	-0.6009	-5.52887
С	1.363518	0.744436	-5.20449
Н	1.410451	1.498618	-5.98226
С	1.111748	1.113336	-3.88619
Н	0.956568	2.15844	-3.64105
C	-1.82739	0.374018	-2.87781
C	-1.90642	-0.59036	-3.89244
Н	-1.73498	-1.63403	-3.64894
С	-2.18108	-0.22056	-5.20906
Н	-2.20903	-0.97841	-5.98624
C	-2.40522	1.119692	-5.53035
Н	-2.6217	1.405883	-6.55534
C	-2.35269	2.086649	-4.52578
Н	-2.53782	3.130597	-4.76291

С	2 06765	1 715758	2 21152
C	-2.00703	1./13/38	-3.21133
Н	-2.03479	2.469496	-2.43
С	1.726257	-1.01088	-6.96364
F	2.466137	-2.13574	-7.08662
F	2.32457	-0.04821	-7.70055
F	0.530614	-1.2658	-7.5537

Table S7: Optimized geometry of triplet state in F-rubrene.

Atom	Х	Y	Z
С	0.842929	0.519802	1.423021
С	2.025897	0.966892	0.714574
С	3.205379	1.346009	1.388032
Н	3.230904	1.319167	2.469753
С	4.34552	1.747813	0.697189
Н	5.232824	2.042898	1.249015
С	-5.09876	-1.19446	0.697236
Н	-5.98258	-1.50032	1.248899
С	-3.96408	-0.77799	1.38847
Н	-3.98842	-0.74867	2.470103
С	-2.78906	-0.38694	0.714408
С	-1.61227	0.073658	1.425568
С	-0.38473	0.296268	0.738533
С	1.039054	0.131415	2.854822
С	1.181117	-1.2318	3.159835
Н	1.098216	-1.96385	2.362579
С	1.421219	-1.65493	4.464156
Н	1.527276	-2.71143	4.686101
С	1.530716	-0.71414	5.489987
С	1.421044	0.648047	5.199384
Н	1.515467	1.378481	5.995379
С	1.187813	1.064284	3.892061
Н	1.090062	2.122678	3.675875
С	-1.81616	0.46998	2.855078
С	-1.96343	-0.45608	3.899039
Н	-1.84744	-1.51504	3.69153
С	-2.22309	-0.02969	5.201181
Н	-2.30029	-0.76034	6.000811
С	-2.3672	1.331004	5.479678
Н	-2.57331	1.661397	6.493449
C	-2.24564	2.261674	4.447253
Н	-2.36569	3.321978	4.651353

С	-1.97097	1.834582	3.148041
Н	-1.87916	2.560982	2.345786
С	1.682945	-1.16818	6.913616
F	2.345659	-2.34301	7.004879
F	2.350079	-0.26544	7.667141
F	0.476784	-1.35502	7.507537
С	0.842929	0.519802	-1.42302
С	2.025897	0.966892	-0.71457
С	3.205379	1.346009	-1.38803
Н	3.230904	1.319167	-2.46975
С	4.34552	1.747813	-0.69719
Н	5.232824	2.042898	-1.24902
С	-5.09876	-1.19446	-0.69724
Н	-5.98258	-1.50032	-1.2489
С	-3.96408	-0.77799	-1.38847
Н	-3.98842	-0.74867	-2.4701
С	-2.78906	-0.38694	-0.71441
С	-1.61227	0.073658	-1.42557
С	-0.38473	0.296268	-0.73853
С	1.039054	0.131415	-2.85482
С	1.181117	-1.2318	-3.15984
Н	1.098216	-1.96385	-2.36258
С	1.421219	-1.65493	-4.46416
Н	1.527276	-2.71143	-4.6861
С	1.530716	-0.71414	-5.48999
С	1.421044	0.648047	-5.19938
Н	1.515467	1.378481	-5.99538
С	1.187813	1.064284	-3.89206
Н	1.090062	2.122678	-3.67588
C	-1.81616	0.46998	-2.85508
C	-1.96343	-0.45608	-3.89904
Н	-1.84744	-1.51504	-3.69153
С	-2.22309	-0.02969	-5.20118
Н	-2.30029	-0.76034	-6.00081
С	-2.3672	1.331004	-5.47968
Н	-2.57331	1.661397	-6.49345
С	-2.24564	2.261674	-4.44725
Н	-2.36569	3.321978	-4.65135
С	-1.97097	1.834582	-3.14804
Н	-1.87916	2.560982	-2.34579
C	1.682945	-1.16818	-6.91362
F	2.345659	-2.34301	-7.00488
F	2.350079	-0.26544	-7.66714
F	0.476784	-1.35502	-7.50754

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