Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information (ESI)

Singlet fission from upper excited singlet states and polaron formation in rubrene film

Tong Wu, [a] Wenjun Ni, [a] Gagik G. Gurzadyan *[a] and Licheng Sun *[abc]

[a] State Key Laboratory of Fine Chemicals, Institute of Artificial Photosynthesis, Dalian University of Technology, 116024 Dalian, China
[b] Department of Chemistry, School of Engineering Sciences in Chemistry, Biotechnology and Health, KTH Royal Institute of Technology, 10044 Stockholm, Sweden
[c] Center of Artificial Photosynthesis for Solar Fuels, School of Science, Westlake University, 310024, Hangzhou, China

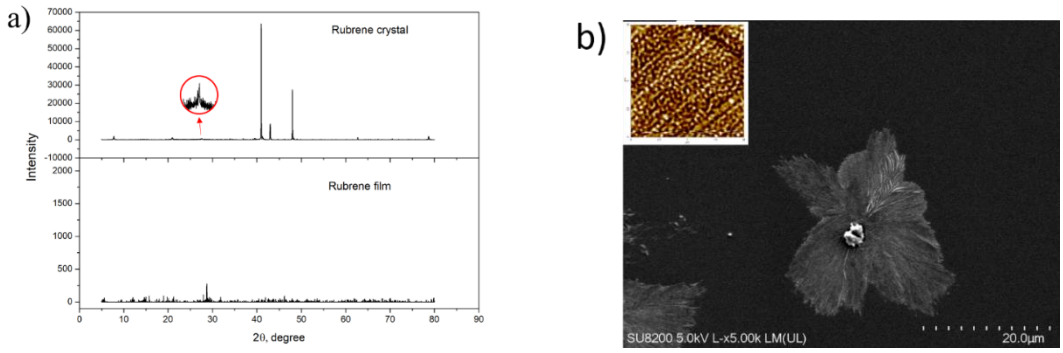

Fig. S1 (a) XRD patterns of rubrene crystal and film, (b) SEM image of rubrene film. 10×10 μm^2 AFM image is shown as an inset.

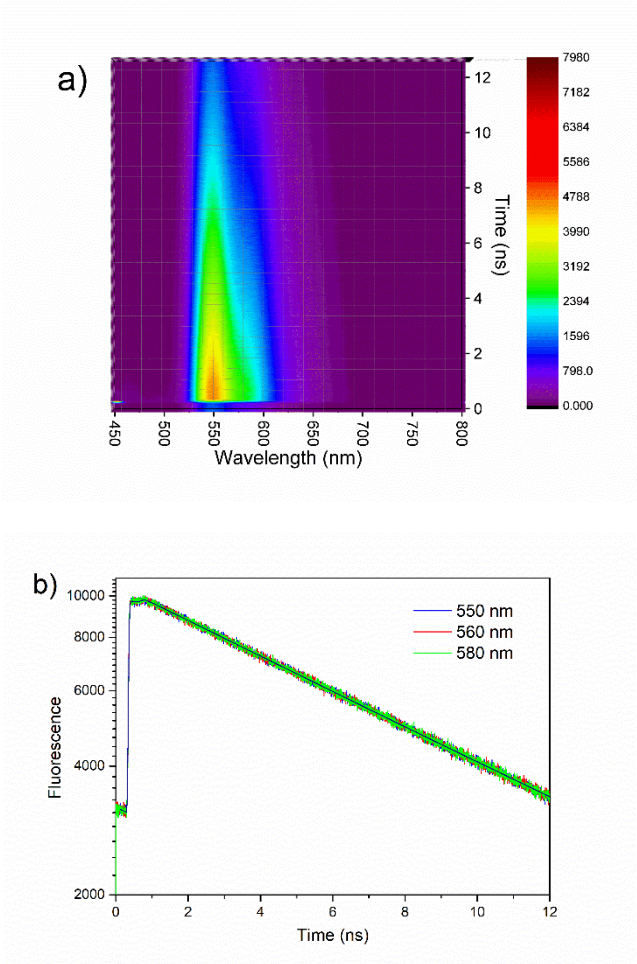

Fig. S2 Fluorescence map (a) and decay kinetics (b) of rubrene in hexane at λ_{ex} = 400 nm.

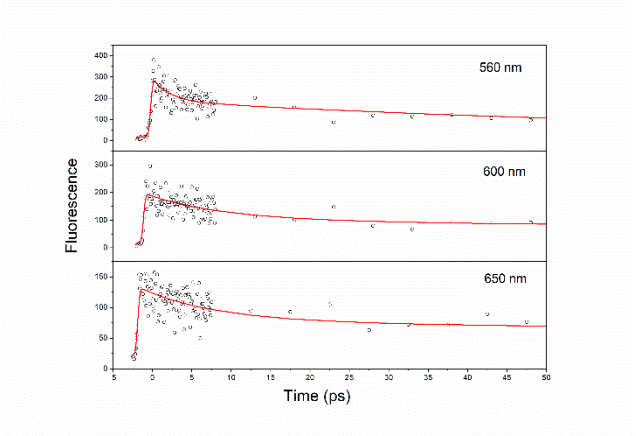

Fig. S3 Up conversion kinetics of rubrene film at different probe wavelengths, λ_{ex} = 400 nm.

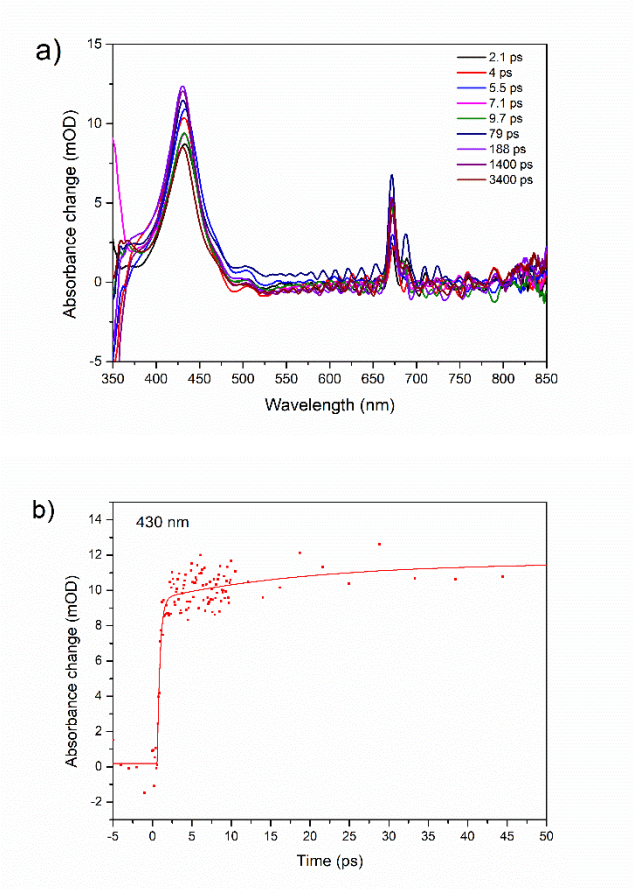

Fig. S4 (a) Femtosecond transient absorption spectra for rubrene in hexane solution at λ_{ex} = 340 nm. (b) Transient kinetics at 430 nm.

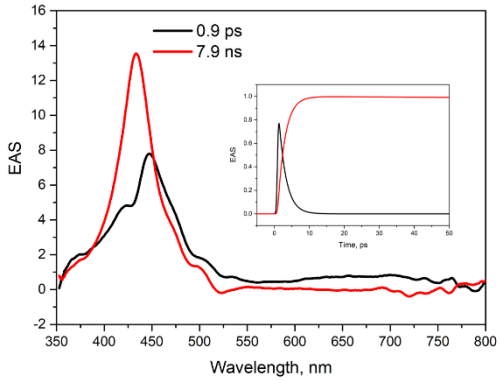

Fig. S5 Global fit spectra of TA measurements in rubrene solution, λ_{ex} = 250 nm. Kinetics is shown as an inset.

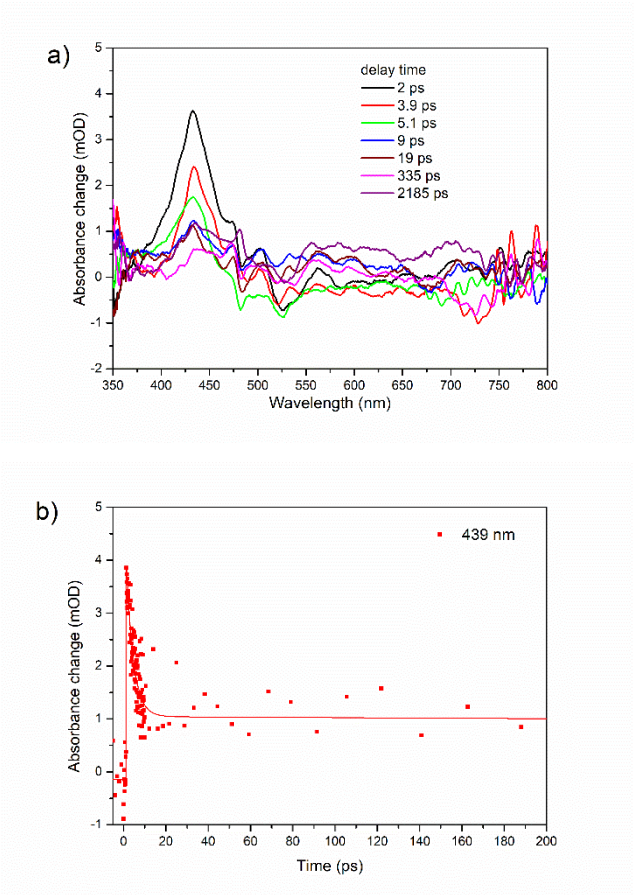

Fig. S6 (a) Femtosecond transient absorption spectra for rubrene film, λ_{ex} = 480 nm. (b) Transient kinetics at 439 nm.

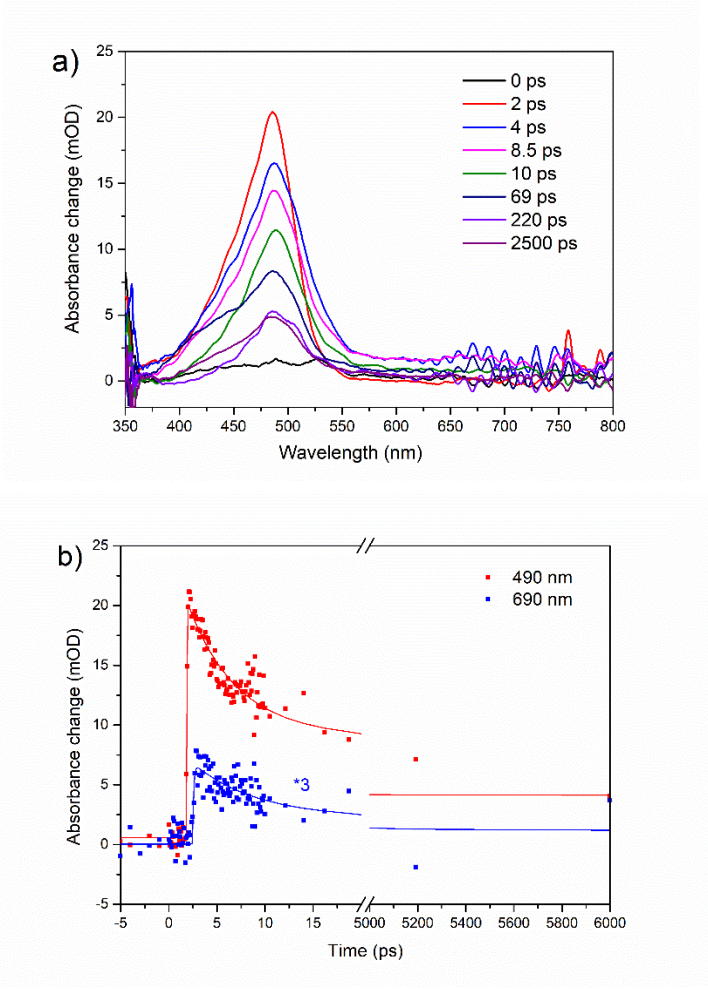

Fig. S7 (a) Femtosecond transient absorption spectra for rubrene film at λ_{ex} = 340 nm, pump fluence: 7.60x10^{-4} J/cm^2. (b) Transient kinetics at different wavelengths.

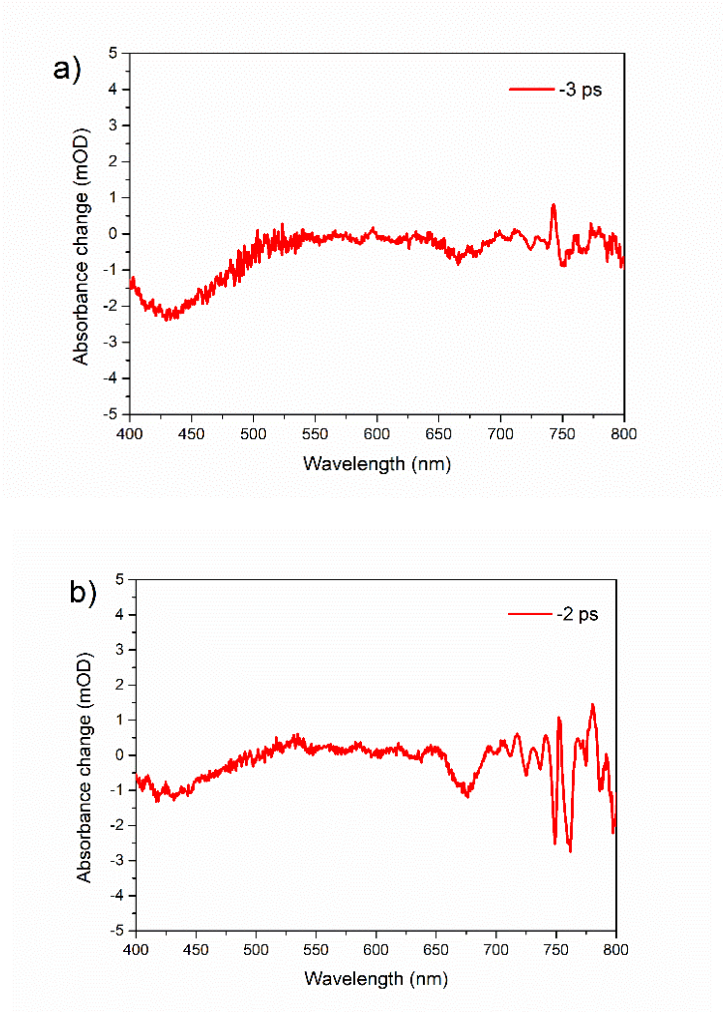

Fig. S8 Transient absorption spectra for rubrene film at minus delay under (a) λ_{ex} = 340 nm and (b) λ_{ex} = 250 nm.

Table S1. Lifetimes obtained from the fit/deconvolution of TCSPC and up-conversion dynamics in rubrene film.

Set up	λ_{ex}, nm	λ_{probe}, nm	τ_1, ps	A_1	τ_2, ps	A_2	τ_3, ps	A_3
TCSPC	400	450	58	0.78	380	0.17	2100	0.04
		460	55	0.75	360	0.20	2200	0.05
		480	55	0.70	400	0.23	2300	0.07
		500	67	0.68	450	0.24	2300	0.07
		520	68	0.66	580	0.21	3700	0.13
		540	110	0.50	750	0.28	4500	0.21
		560	190	0.33	1100	0.40	4600	0.27
		580	230	0.24	1200	0.47	4900	0.29
		600	220	0.28	1200	0.44	4600	0.30
		620	340	0.23	1400	0.49	5300	0.28
		640	380	0.21	1400	0.49	5100	0.30
		660	340	0.24	1400	0.50	5000	0.26
TCSPC	266	350	9	1				
		400	10	1				
		450	10	1				
		500	33	0.82	170	0.16	830	0.02
		520	32	0.64	150	0.34	830	0.02
		540	60	0.70	190	0.25	1100	0.05
		560	61	0.43	190	0.46	1100	0.10
		580	81	0.48	270	0.42	1300	0.10
		600	100	0.52	310	0.38	1400	0.10
		620	100	0.50	340	0.41	1500	0.09
		640	110	0.52	360	0.39	1600	0.07
		660	110	0.52	380	0.40	1500	0.08
		680	110	0.47	380	0.45	1500	0.08
		700	110	0.48	380	0.44	1500	0.08
Up-conversion	400	500	2.2	0.53	29	0.47		
		540	7.4	0.65	180	0.35		
		560	2.2	0.41	76	0.59		
		580	7.7	0.55	210	0.45		
		600	9.6	0.54	280	0.46		
		630	1.4	0.25	110	0.75		
		650	9.2	0.50	280	0.50		
		670	2.3	0.24	100	0.76		

Table S2. Lifetimes obtained from the fit/deconvolution of femtosecond transient absorption spectra of rubrene film; f = fixed.

λ_{ex}, nm	λ_{probe}, nm	τ_1, ps	A_1	τ_2, ps	A_2	τ_3, ps	A_3
250	441	0.24	0.37	6.7	0.36	3400	0.27
	486	3.1	0.55	140	0.25	100000[f]	0.20
	706	2.0	0.51	23	0.25	100000[f]	0.24
340	441	7.6	0.57	460	0.13	8400	0.30
	490	5.0	0.56	220	0.25	100000[f]	0.19
	690	0.11	-0.98	6.8	0.65	9800	0.35
400	439	5.0	0.47	56	0.07	4200	0.46
	489	29	0.34	2400	0.25	100000[f]	0.41
480	439			3.4	0.71	5700	0.29

TDDFT calculations of rubrene

Singlet excited states of rubrene calculated by TDDFT/B3LYP/6-31G(d) level with Gaussian 09W, based on the optimized ground state geometries.

Singlet state	Energy, eV	Oscillator strength
S1	2.18	0.1599
S2	3.22	0.0047
S3	3.28	0.0078
S4	3.40	0.0001
S5	3.51	0.0079
S6	3.67	0.0160
S7	3.71	0.0198
S8	3.79	0.0000
S9	3.81	0.0000
S10	3.84	0.0000
S11	4.01	0.0033

S12	4.06	0.5000
S13	4.12	0.0032
S14	4.14	0.0641
S15	4.15	0.0046
S16	4.18	0.3283
S17	4.19	0.0000
S18	4.25	0.0008
S19	4.28	0.0041
S20	4.34	0.0000
S21	4.54	0.0003
S22	4.55	0.8489
S23	4.66	0.0000
S24	4.89	0.0049
S25	4.96	0.0021
S26	4.98	0.1030
S27	4.99	0.0000
S28	5.03	0.0000
S29	5.05	0.0719
S30	5.11	0.0000

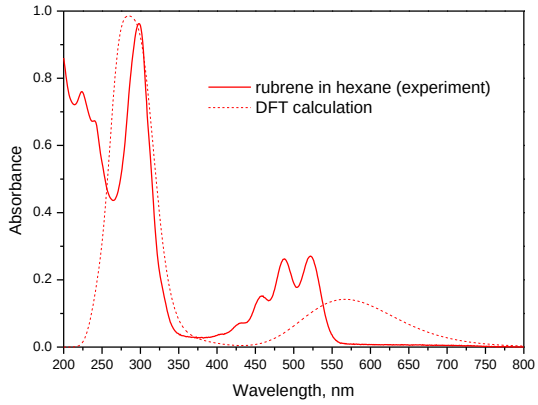

Fig. S9 Experimental and simulated absorption spectra of rubrene.

Triplet excited states of rubrene calculated by TDDFT/B3LYP/6-31G(d) level with Gaussian 09W, based on the optimized ground state geometries.

Triplet state	Energy, eV	Oscillator strength
T1	0.95	0.0000
T2	2.32	0.0000
T3	2.97	0.0000
T4	3.07	0.0000
T5	3.27	0.0000
T6	3.27	0.0000
T7	3.28	0.0000
T8	3.38	0.0000
T9	3.57	0.0000
T10	3.61	0.0000
T11	3.70	0.0000
T12	3.73	0.0000
T13	3.75	0.0000
T14	3.79	0.0000
T15	3.80	0.0000

T16	3.82	0.0000
T17	3.89	0.0000
T18	3.91	0.0000
T19	3.98	0.0000
T20	4.02	0.0000
T21	4.06	0.0000
T22	4.07	0.0000
T23	4.08	0.0000
T24	4.20	0.0000
T25	4.21	0.0000
T26	4.26	0.0000
T27	4.30	0.0000
T28	4.31	0.0000
T29	4.33	0.0000
T30	4.44	0.0000
T31	4.56	0.0000
T32	4.58	0.0000

Singlet excited states of rubrene calculated by TDDFT/CAM-B3LYP/6-31G(d) level with Gaussian 09W, based on the optimized ground state geometries.

Singlet state	Energy, eV	Oscillator strength
S1	2.61	0.2346
S2	3.51	0.0020
S3	4.00	0.0294
S4	4.30	0.0002
S5	4.39	0.0032

S6	4.46	0.0120
S7	4.60	1.7209
S8	4.65	0.0313
S9	4.83	0.0000
S10	4.90	0.0002
S11	4.96	0.0000
S12	5.03	0.0000
S13	5.09	0.0256
S14	5.11	0.0467
S15	2.19	0.0010

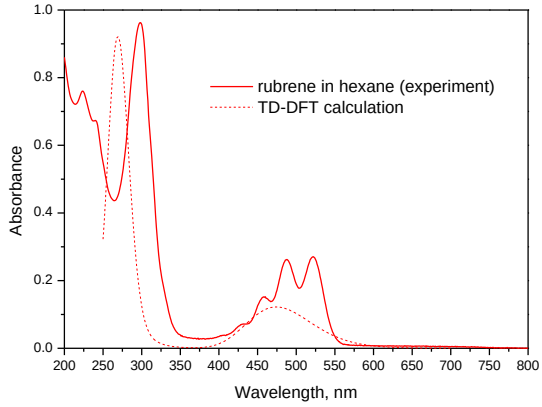

Fig. S10 Experimental and simulated absorption spectra of rubrene.

Triplet excited states of rubrene calculated by DFT/B3LYP/6-31G(d) level with Gaussian 09W, based on the optimized ground state geometries.

Triplet state	Energy, eV	Oscillator strength
T1	0.63	0.0000
T2	2.31	0.0000
T3	3.26	0.0000
T4	3.29	0.0000

T5	3.38	0.0000
T6	3.40	0.0000
T7	3.42	0.0000
T8	3.54	0.0000
T9	3.56	0.0000
T10	3.86	0.0000
T11	4.12	0.0000
T12	4.27	0.0000
T13	4.30	0.0000
T14	4.31	0.0000
T15	4.45	0.0000
T16	4.61	0.0000
T17	4.63	0.0000
T18	4.65	0.0000
T19	4.70	0.0000
T20	4.72	0.0000
T21	4.74	0.0000
T22	4.75	0.0000
T23	4.77	0.0000
T24	4.77	0.0000
T25	4.84	0.0000
T26	4.88	0.0000
T27	4.90	0.0000
T28	4.97	0.0000
T29	4.99	0.0000
T30	5.02	0.0000

T31	5.10	0.0000
T32	5.24	0.0000