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 ** 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 μm² AFM image is shown as an inset.

**Fig. S2** Fluorescence map (a) and decay kinetics (b) of rubrene in hexane at λ<sub>ex</sub> = 400 nm.
**Fig. S3** Up conversion kinetics of rubrene film at different probe wavelengths, $\lambda_{ex} = 400$ nm.

**Fig. S4** (a) Femtosecond transient absorption spectra for rubrene in hexane solution at $\lambda_{ex} = 340$ nm. (b) Transient kinetics at 430 nm.
**Fig. S5** Global fit spectra of TA measurements in rubrene solution, $\lambda_{ex} = 250$ nm.

Kinetics is shown as an inset.

**Fig. S6** (a) Femtosecond transient absorption spectra for rubrene film, $\lambda_{ex} = 480$ nm.

(b) Transient kinetics at 439 nm.
Fig. S7 (a) Femtosecond transient absorption spectra for rubrene film at $\lambda_{ex} = 340$ nm, pump fluence: $7.60 \times 10^{-4}$ J/cm$^2$. (b) Transient kinetics at different wavelengths.
Fig. S8 Transient absorption spectra for rubrene film at minus delay under (a) $\lambda_{\text{ex}} = 340$ nm and (b) $\lambda_{\text{ex}} = 250$ nm.
Table S1. Lifetimes obtained from the fit/deconvolution of TCSPC and up-conversion dynamics in rubrene film.

| Set up | $\lambda_{\text{ex}}, \text{nm}$ | $\lambda_{\text{probe}}, \text{nm}$ | $\tau_1, \text{ps}$ | $A_1$ | $\tau_2, \text{ps}$ | $A_2$ | $\tau_3, \text{ps}$ | $A_3$ |
|--------|-----------------|-----------------|-----------------|-----|-----------------|-----|-----------------|-----|
| 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            |     |
|        | 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              | 0.60            | 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            |     |
|        | 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.

| \( \lambda_{\text{ex}}, \text{nm} \) | \( \lambda_{\text{probe}}, \text{nm} \) | \( \tau_1, \text{ps} \) | \( A_1 \) | \( \tau_2, \text{ps} \) | \( A_2 \) | \( \tau_3, \text{ps} \) | \( A_3 \) |
|---|---|---|---|---|---|---|---|
| 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              |
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              |
| T  |  Value | Error |
|----|--------|-------|
| 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 |