

# Temperature-dependent singlet exciton fission observed in amorphous rubrene films



Jing Li, Zhonghai Chen, Qiaoming Zhang, Zuhong Xiong\*, Yong Zhang\*

School of Physical Science and Technology, Southwest University, Chongqing 400715, PR China

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## ABSTRACT

The steady-state/transient fluorescence spectroscopy was used to demonstrate that the dynamics of singlet exciton fission in amorphous rubrene were temperature-dependent (50–300 K). Based on the traditional three-state model of singlet fission, time-resolved fluorescence decay curves measured at different temperatures could be well fitted by using a set of rate equations. The variations of specific rate constants were consistent with the conventional Arrhenius-type, thermally activated process. Additionally, the magnetic field effect of photoluminescence was apparently suppressed at low temperatures. All these findings offer clear evidence that the amorphous rubrene solid undergoes thermally activated singlet exciton fission due to the endothermic nature of fission process in rubrene.

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## 1. Introduction

Singlet exciton fission observed in organic solid is a spin-allowed process in which an excited high energy singlet exciton ( $S_1$ ) shares its half of energy with another molecule at ground state ( $S_0$ ), and subsequently both of them convert into a pair of low energy triplet excitons ( $T_1$ ). In the past few years, singlet fission became a scientific hotspot in the field of physics, chemistry, and organic electronics (see Ref. [1,2] for recent reviews). Generally, singlet fission can be regarded as a carrier multiplication process in which two electron-hole pairs are created. If all of the charges can be efficiently collected, the photocurrent of device will be effectively enhanced. Therefore, it was suggested that organic molecules with fission property can be used as a new type of sensitizer to improve the quantum efficiency of organic photovoltaic devices [3–8].

Generally, the energies of  $S_1$  and  $T_1$  states must fulfill the requirement of  $E(S_1) \approx 2E(T_1)$  for fission process to occur. For instance,  $E(S_1) - 2E(T_1) = 0.11$  eV in pentacene [9],  $E(S_1) - 2E(T_1) = -0.18$  eV in tetracene [10,11], and  $E(S_1) - 2E(T_1) = -0.05$  eV in rubrene [12]. Ultrafast fission processes have been observed in these materials. It was found by Thorsmølle et al. that there was no temperature dependence in the fission process of pentacene since  $E(S_1) > 2E(T_1)$  in pentacene [9]. However, Wilson et al. demonstrated that singlet fission in tetracene crystal was also independent of temperature

although  $E(S_1) < 2E(T_1)$  in tetracene [13]. The above two results constitute an important scientific puzzle that whether or not singlet fission should be temperature-independent for exothermic case and temperature-dependent if it is endothermic. Although researchers have made a lot of effort [9,14–16], more explicit experimental results are still required in order to elucidate this basic question.

In this work, highly efficient fission material, i.e., 5,6,11,12-tetraphenyltetracene (rubrene) was deposited by using thermal evaporation, forming amorphous rubrene films. Steady state/transient photoluminescence (PL) and magneto-photoluminescence (MPL) were measured in a wide range of temperature. In both PL and MPL measurements, we found that singlet fission in amorphous rubrene was temperature-dependent. For instance, at temperature of 300 K, the transition rate in singlet fission was fitted to be  $\sim 0.5$  ns<sup>-1</sup>. However, the fission rate was almost completely suppressed at temperatures lower than 50 K, confirming that singlet fission in amorphous rubrene was a thermally activated process. This is in line with the endothermic nature of singlet fission in rubrene material.

## 2. Experimental

Rubrene films of 100 nm thick were thermally evaporated on the glass substrates at high vacuum about  $1 \times 10^{-6}$  Pa. It is generally found by different researchers that the obtained rubrene films usually exhibit amorphous morphology [16–18]. Park et al. observed the growth of island-like crystalline domains only after annealing the films at higher-than-room temperatures [18]. However, mixed amorphous/crystalline phases probably appear

\* Corresponding authors.

E-mail addresses: [zhxiong@swu.edu.cn](mailto:zhxiong@swu.edu.cn) (Z. Xiong), [yzh6127@swu.edu.cn](mailto:yzh6127@swu.edu.cn) (Y. Zhang).

in rubrene films after preparation [19]. In order to eliminate the possible coexistence of amorphous and crystalline domains, the substrates were kept at room temperature during deposition process and the deposition rate was always controlled at 0.5 Å/s. The fresh samples were saved in a vacuum chamber (better than  $1 \times 10^{-2}$  Pa) and measured within 12 h. The PL spectra and time-resolved fluorescence decay were measured by using an Edinburgh FLS920 steady-state/transient fluorescence spectrometer with cryostat. Rubrene films were excited by monochromatic light ( $\lambda = 355$  nm) from a nanosecond flash lamp operated at 2 MHz. The minimal pulse width of excitation was about 800 ps. When measuring the MPL effect in steady-state, rubrene samples were mounted on the cold finger of another cryostat which was located between the pole pieces of an electromagnet [20]. Photoluminescence from rubrene films was excited by using a semiconductor laser with 405 nm wavelength. The output power of laser was tuned within 1–5 mW. And the focal size of laser spot on the sample was about 1.5 mm in diameter. During all the above measurements, the samples were held in vacuum which is better than  $1 \times 10^{-2}$  Pa. Under the above conditions, we were able to obtain consistent measurement results. Apparent fluctuations in the rates of singlet fission and amplitudes of MPL effect were not observed.

### 3. Results and discussions

For a comparison with rubrene solid, the insert of Fig. 1 shows the spectra of another sample in which rubrene molecules was doped in *N, N'*-Di(naphthalen-1-yl)-*N, N'*diphenyl-benzidine (NPB) material. The doping concentration was about 3% by weight ratio. Supposing that the doped rubrene molecules were almost uniformly distributed in the NPB matrix, the averaged intermolecular distance between adjacent rubrene molecules could be estimated to be about 2.9 nm [20]. Although the height of fluorescence peak around 565 nm slightly rose when temperature was decreased, actually the area under each spectral line was almost constant. During measurement process, the intensity of light excitation was kept unchanged. In addition, no magnetic field effect of photoluminescence could be measured. This confirmed that fission process could not occur in this sample because of the large averaged intermolecular distance.

Jankus et al. investigated the excited state dynamics in amorphous rubrene films [16]. They determined the fission rate to be

$>2.5 \times 10^{12} \text{ s}^{-1}$  and proposed that the temperature-dependent polaron pair formation from singlet excitons could compete with singlet fission. Similarly, if charge dissociation plays an important role in the decay of photoexcited singlet excitons, we should be able to observe this effect in NPB: rubrene (3%) composite film. Since HOMO (highest occupied molecular orbit) levels of NPB and rubrene are almost the same ( $\sim 5.4$  eV), the photogenerated holes could migrate from rubrene molecules to NPB matrix. However, we found that the time-resolved fluorescence decays measured at different temperatures were almost the same in NPB: rubrene (3%) sample. This indicated that the thermally excited singlet dissociation process could actually be excluded in our analysis.

The fluorescence spectra of amorphous rubrene film recorded at different temperatures are shown in Fig. 1. At 300 K, the maximum of spectrum around  $\lambda = 565$  nm was normalized to be 1. With decreasing temperature, the PL intensity became stronger and stronger. At 50 K, the maximum of spectrum at  $\lambda = 577$  nm substantially increased up to  $\sim 18$ . In pure rubrene film, we can generally assume that singlet fission (rate constant can be expressed as  $k_{\text{fiss}}$ ) and singlet recombination (including radiative and other non-radiative recombination processes, total rate constant can be expressed as  $k_{\text{S}}$ ) are two dominant quenching pathways for photoinduced singlet excitons whereas singlet dissociation and intersystem crossing are negligible. Therefore, the PL intensity  $F_{\text{PL}}$  in steady-state is usually proportional to the ratio of  $k_{\text{S}}/(k_{\text{S}} + k_{\text{fiss}})$ . If the value of  $k_{\text{S}}$  is unchanged, then the considerably increased PL intensity as shown in Fig. 1 could be mainly attributed to the suppression of  $k_{\text{fiss}}$  at low temperatures [20]. This implied that singlet fission in amorphous rubrene could be a thermally activated process.

In order to investigate the microscopic dynamics of singlet fission in amorphous rubrene, we measured the transient fluorescence decays at different temperatures. At each temperature, the peak wavelength in spectrum was located and its time-resolved fluorescence decay was taken. For NPB: rubrene (3%) composite film, all decay curves are almost identical, thus only the curve measured at 300 K is shown in Fig. 2. Within about 0–30 ns, it could be approximately regarded as a mono-exponential decrease. Hence, constant decay rate of singlet excitons (including radiative recombination and other temperature-independent non-radiative loss),

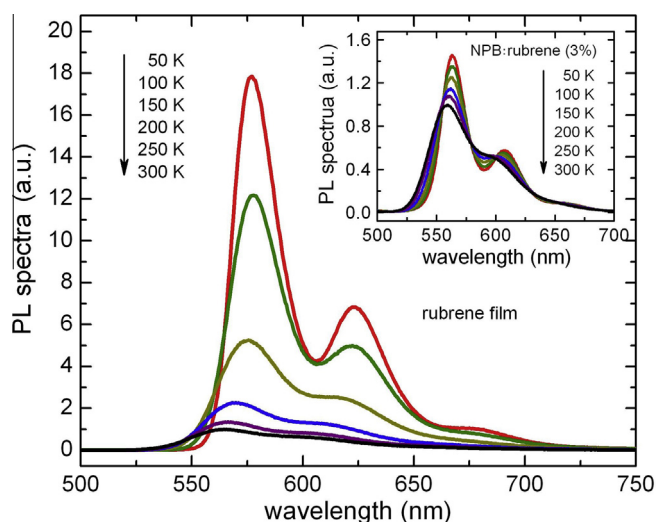


Fig. 1. Fluorescence spectra of rubrene films measured at different temperatures. The insert shows the spectra of a rubrene-doped sample (NPB: rubrene, 3% by weight ratio).

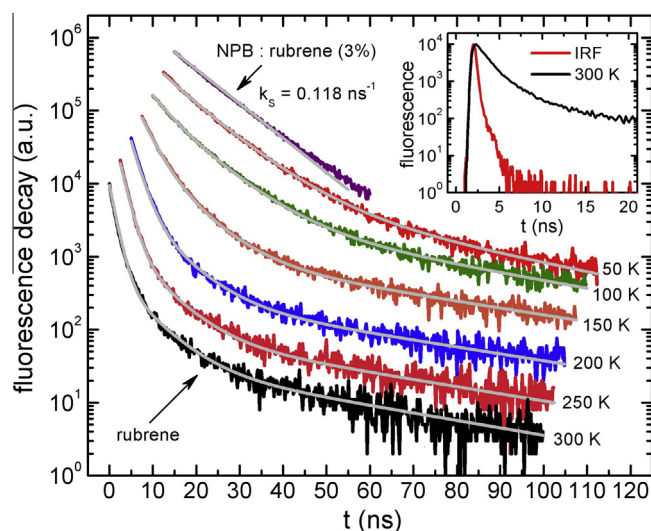


Fig. 2. Time-resolved fluorescence decays of rubrene films measured at different temperatures. Offsets are applied to avoid overlapping. All the curves were fitted by using coupled rate equations. The fluorescence decay of rubrene-doped sample is also shown. The insert shows the measured instrument response function (IRF).

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