Nonlinear Density Dependence of Singlet Fission Rate in Tetracene Films

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ABSTRACT: Singlet fission holds the potential to dramatically improve the efficiency of solar energy conversion by creating two triplet excitons from one photoexcited singlet exciton in organic semiconductors. It is generally assumed that the singlet-fission rate is linearly dependent on the exciton density. Here we experimentally show that the rate of singlet fission has a nonlinear dependence on the density of photoexcited singlet excitons in tetracene films with small crystalline grains. We disentangle the spectrotemporal features of singlet and triplet dynamics from ultrafast spectroscopic data with the algorithm of singular value decomposition. The correlation between their temporal dynamics indicates a superlinear dependence of fission rate on the density of singlet excitons, which may arise from excitonic interactions.

SECTION: Spectroscopy, Photochemistry, and Excited States
fluorescence (TRFL) spectra. Recently, Burdett and Bardeen
have thoroughly reexamined the quantum beats in the delayed
fluorescence of crystalline tetracene,\textsuperscript{31,32} which has been
regarded as a fingerprint of SF.\textsuperscript{3,25} A typical TRFL trace of
the sample is shown in Figure 1a. By subtracting the
multieponential decay component, the oscillations emerge as
shown in the inset of Figure 1a. The Fourier transformation of
the oscillatory components shows three peaks at 1.07, 1.84, and
2.95 GHz in the frequency domain (Figure 1b). These values
are in good agreement with the theoretical prediction of energy
separations between manifolds of the triplet-pair states,\textsuperscript{3,25}
indicating the presence of triplet pairs generated from SF in
the sample.

The exciton dynamics in crystalline tetracene may be
strongly affected by many body interactions such as the
singlet–singlet annihilation (SSA) and triple–triplet annilha-
tion (TTA) when the density of excitons is high.\textsuperscript{3,16,25} We
conduct power-dependent TA experiments to determine the
linear power regime. The pump–probe traces probed at 2.34
eV with different power excitation at 3.1 eV are presented in
Figure 2a. No significant power dependence has been observed
with exciton fluence <30 µJ/cm\textsuperscript{2}, which is similar to previous
results.\textsuperscript{16,25} Nonetheless, the early stage dynamics in the linear
regime is dominated by a component with lifetime <30 ps,
which is much faster than that in the literature.\textsuperscript{3,25} This is
probably caused by the trapping effect in our samples with
small crystalline grains. We characterize the morphology of the
film by atomic force microscopy. As shown in Figure 2b, the
diameters of grains are about ~100 nm, which is about 5 times
smaller than that in the previous study.\textsuperscript{3} More trapping centers
may be introduced due to over 2 orders of magnitude
enhancement in surface-to-volume ratio in the sample. It may
strongly affect the exciton dynamics in polyacene materials.\textsuperscript{2,3}

The measured ΔT/T in the 1.3–2.6 eV spectral region
within a temporal window of 3 ns monitors the dynamics of the
SF process (Figure 3a). The excitation power is set to be ~5
µJ/cm\textsuperscript{2} (carrier density, ~2 × 10\textsuperscript{17} cm\textsuperscript{−3}) in the linear regime.\textsuperscript{106}
The transient optical response consists of multiple entangled
components such as stimulated emission, ground-state
bleaching, excited-state absorption, and so on. In tetracene,
the transitions of S\textsubscript{0} → S\textsubscript{1}, S\textsubscript{1} → S\textsubscript{2}, and T\textsubscript{1} → T\textsubscript{2}
are responsible for the measured TA signal.\textsuperscript{3,16,19} However, it is challenging to
effectively assign the transient features at single wavelengths to
specific transitions. In the current study, the major bands of
photoinduced bleaching and absorption locate at ~2.3 eV and
~1.8 eV (Figure 3a), respectively. Their instant build-up
processes as well as the fast decays at early stage (Figures 3b,c)
are the characteristics of singlet excitons.\textsuperscript{3,19} Nevertheless, the
long-lived tails, with the amplitude ratios much larger than that
exhibited in the TRFL curves, imply that the triplet excitons
may also make some contributions.

The spectrotemporal features for the triplet excitons are
more complicated. In general, triplet excitons are characterized
by long-lived signals of photoinduced absorption. Such features
have been reported with probe energies at 1.67 eV,\textsuperscript{3,19} 2.53 eV,\textsuperscript{24}
and 2.67 eV\textsuperscript{16} in different studies, respectively. Here, a similar
long-lived band of photoinduced absorption appears at ~1.60
eV. This component becomes prominent after ~100 ps and
remains largely static in the time scale between 0.1 and 3 ns,
which has been regarded as a clear signature of SF in crystalline
tetracene.\textsuperscript{3,19} The build-up process consists of one subpico-
second component and one delayed-rising component (Figure
3d). Thorsmølle et al. assigned the two components to exciton
fission from higher (S\textsubscript{0} → 2T\textsubscript{1}) and lowest singlet states (S\textsubscript{1} →
2T\textsubscript{1}), respectively.\textsuperscript{3} Wilson et al. proposed an alternative
explanation that the subpicosecond rise is also contributed by
singlet excitons.\textsuperscript{19}
For a better assignment, we employ the established algorithm of SVD to disentangle the spectrotometrical features of singlet and triplet excitons. The detailed description of SVD is available in the Supporting Information. This method has been successfully used in extracting both energy- and time-domain information from a set of data in several research areas.34–39 Here, we approximately adopt the signals at t ∼ 0.5 ps and t ∼ 3 ns as the spectral features to extract the temporal dynamics of the singlet and triplet excitons, respectively.40 Such SVD approach has well reproduced the experimental data as compared in Figure 4a,b. The reconstructed dynamics of singlet and triplets are plotted in Figure 4c. The dynamics probed at single wavelengths (i.e., 1.6 eV) can be regarded as a combination of the singlet and triplet dynamics, which is further confirmed by the excitation-wavelength dependent experiments (Supporting Information).

The dynamics of singlet and triplet population can be expressed in a set of rate equations as

\[ \frac{dN_S(t)}{dt} = -k_{SF}N_S(t) - k_{SS}N_S(t) - k_{SS}N_T(t) + k_{TT}N_T(t) \]

(1)

\[ \frac{dN_T(t)}{dt} = 2k_{SF}N_S(t) - k_{SF}N_T(t) - k_{TT}N_T(t) \]

(2)

where \( k_{SF}, k_{SS}, k_{SS}, k_{SF} \) and \( k_{TT} \) are the rate constants for SF, spontaneous recombination of singlet excitons (including spontaneous emission and nonradiative recombination like defect trapping), SSA, spontaneous recombination of triplet excitons, and TTA, respectively. Unlike the case of a single crystal (Supporting Information), it is difficult to reproduce the curves recorded from the film with the available rate equations16 or the model used in Wilson’s paper.19

We try to directly connect the fission rate with the dynamics of singlet excitons. Since spontaneous recombination of triplet excitons and TTA are very slow, only the process of SF is responsible for the early stage dynamics of triplet excitons (t < 100 ps), i.e.,

\[ \frac{dN_T(t)}{dt} \approx 2k_{SF}N_S(t) \]

(3)

As deduced in the Supporting Information, the temporal differential of triplet density \( (dN_T(t)/dt) \), i.e., the SF rate, is proportional to the value of \( N_T(0) - N_T(t) \) (\( N_T(0) \) is the maximum density of triplet excitons) (inset, Figure 5a). We compare its temporal evolution with the dynamics of singlet excitons in Figure 5. Surprisingly, the curve of \( N_T(0) - N_T(t) \) (i.e., \( dN_T(t)/dt \)) shows a significant disparity from the linear dependence \( (N_T(t)) \), but close to the quadratic dependence \( (N_T^2(t)) \), when \( t < 10 \) ps (Figure 5a). This result strongly suggests that, rather than being a constant, \( k_{SS} \) is actually density dependent, i.e., \( k_{SS} = k_{SS}(1 + \alpha N_S) \). That is, the rate of SF is superlinearly dependent on the density of singlet excitons. For a better analysis, we rewrite the triplet dynamics in an integration form as

\[ N_T(t) = \int_0^t 2k_{SF}N_S(r) \, dr \]

(4)

The detailed description of the fitting procedure is available in the Supporting Information. The temporal evolution behavior of the triplet exciton population (Figure 5b) can be well fitted by the superlinear dependence with the parameter \( \alpha \approx 3k_{SF}/N_{SS} \). Roughly speaking, the triplet population generated from the nonlinear channel is \( \sim 1.5 \) times of that from the linear channel. Assuming the time constant for linear channel to be close to the reported value \( (1/k_{SF} \approx 100 \text{ ps}^{-1}) \), the fractions of singlet excitons that undergo the linear and nonlinear fission processes can be approximately estimated to be \( \sim 25\% \) and \( \sim 38\% \), respectively. The overall triplet yield is \( \sim 126\% \) in this sample, which is less efficient than the reported value in regular samples.4,16,23,30 This is reasonable considering the high density of trapping centers in the films with smaller grain sizes.3

Notably, despite the superlinear dependence is deduced in the linear power regime as we discussed above, it is also valid in...
the high power regime. As shown in Figures 5c,d, the onset of
triplet dynamics, obtained by eliminating singlet contribution
from the signal probed at 1.6 eV, can be well produced with
excitation in a high regime with a similar parameter of $\alpha$ where
SSA becomes important. The onset of triplet population is
much better described by the superlinear than the linear
dependence. Nonetheless, further increasing excitation power
leads to a failure of reproducing the experimental data (Figure
5e), which is reasonable since eq 3 is no longer valid in this
regime where TTA becomes important at the early stage.

The intrinsic physics underlying the superlinear density
dependence of SF rate is yet to be elucidated. In general,
second-order rate in population implies a role played by the
interactions between singlet excitons. The process of SSA may
assist the SF in some materials by generating higher energy
excitons.41,42 Nonetheless, SSA has been regarded as a major
channel that competes against SF in tetracene.16,25 The
presence of SSA may lead to a fast onset of triplet signal but
cause a reduction in the triplet yield.41,42 Since the nonlinear
density dependence applies for weak excitation density ($\mu$/
$cm^2$, $\sim 2 \times 10^{17} \text{cm}^{-3}$), other process different from SSA may be
involved. To confirm this, we evaluate the excitation-density-
dependent fission yield by monitoring the relative density of
delayed fluorescence. The results are shown and discussed in
detail in the Supporting Information (Figure S8). The relative
intensity of delayed fluorescence represents the density ratio
between singlet excitons from prompt photo excitation and
from triplet fusion process. The efficiency drop of SF induced
by excitonic annihilation processes (i.e., SSA and TTA) has
been observed with a drop in the relative intensity of delayed
fluorescence when the excitation density surpasses a value of
$\sim 50 \mu$/cm$^2$. Under the regime of weak excitation in this
work ($<50 \mu$/cm$^2$), the relative density of delayed
fluorescence increases with increasing excitation density, which
qualitatively supports the existence of a nonlinear-density-
dependent channel of SF that is different from SSA.

In organic crystals, the coupling between excitons and
intermolecular vibrational modes results in coherently emitting
molecules, leading to the superradiant emission.44–47 The rate
of superradiant recombination exhibits nonlinearity in a low
density regime.48 In crystalline tetracene, these excitations can
delocalize over tens of molecules.44,45 These superradiant
excitons, whose transition dipoles interact with light in a
collective and coherent fashion,45 may be responsible for the SF
with nonlinear density dependence. Previously, superradiant
emission has been observed to be dominant at low temperature,
which diminishes with increasing temperature.44,45 Recent
experiments suggest that the exciton delocalization may be
also important at room temperature to explain the SF
dynamics16 and weak magnetic coupling between triplet
pairs32 in crystalline tetracene. If the fraction of singlet excitons
that undergo nonlinear fission channel is related to the
probability of exciton encounter, the encounter radius can be
roughly estimated to be in the range of 3–10 nm with the
stochastic model.49,50 The scale of delocalization for superradiant
excitons is comparable to the encounter radius, which
may strongly affect the dynamics of SF. Nevertheless, more in-
depth research is required to uncover the relation between
superradiant excitons and the nonlinear-density-dependent SF
in crystalline tetracene. The state-of-art techniques, particularly
the first-principle simulation24 and two-dimensional spectro-
scopic survey on quantum coherence,31,52 may provide the
most relevant information on this issue.

We also perform control experiments on single crystals and
find that the crystalline quality is important. The value of $k_{SS}$ in
single crystals is close to the general case with linear density
dependence (Supporting Information). This discrepancy can be
understood if we consider the coexistence of two pathways of
SF in tetracene, i.e., the linear and nonlinear density-dependent
parts. Due to the structure imperfections, excitons in organic
semiconductors may be trapped by the localized minima which
strongly affect the exciton dynamics.2,3 The trapping effect may
significantly harm the efficiency of SF in polyacene materials.1,4

The densities of trapping centers induced by structure
imperfections (i.e., dislocations and surface states) are much
higher in films with small grain sizes, which may quench the SF
of linear-density-dependent part.3 In this case, triplet
population induced by the nonlinear part can be detected. In
single crystals, the linear part plays a dominant role. This
scenario also explains the observation in the literature that the
amplitude ratios between triplet and singlet signals in
polycrystalline films are much smaller than that in single
crystals.3,16,25

In summary, we have reported a superlinear dependence of SF
rate on the density of photoexcited singlet excitons in tetracene
films with small grain sizes. To elucidate the SF dynamics in
tetracene films, we employed the SVD algorithm to analyze the
ultrafast TA data. The nonlinear density-dependent SF implies
a role played by excitonic interactions. Once the understanding
of exact mechanism is achieved, it may be considered as a new
route to search for efficient SF sensitizers to improve
performance of solar cells and photodetectors.

EXPERIMENTAL METHODS

We prepared the tetracene films with thickness of $\sim$100 nm by
evaporating tetracene powders thermally on precleaned glass
substrates. The sample quality was characterized by X-ray
diffraction and atomic force microscopy. TRFL spectra were
recorded by the technique of time-correlated single-photon
counting with a temporal resolution of $\sim$50 ps. We utilized a
commercial Ti:sapphire regenerative amplifier (Libra, Coher-
tent) at 800 nm (1.55 eV) with a repetition rate of 1 kHz and
pump pulse duration of $\sim$90 fs to carry out the TA experiments. For
broadband measurements, a second-harmonic light source at 305
3.1 eV was used as the pump beam and an optical parametric
amplifier (Opera solo, Coherent) was used to provide a probe
beam with tunable wavelength. The relative polarizations of the
pump and probe beams were set to be at the magic angle
($54.7^\circ$). We used balance detection scheme together with a
lock-in amplifier to measure the fractional change in trans-
mission ($\Delta T/T$) with a resolution of $\sim 10^{-5}$. The experiments
were performed with samples in vacuum provided by a cryostat
(MicroCryostatHe, Oxford).

ASSOCIATED CONTENT

Supporting Information

Detailed information concerning experimental procedures, data
analysis techniques, and extra experimental data. This material
is available free of charge via Internet at http://pubs.acs.org.

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(40) The density of singlet exciton at ∼3 ns is over 2 orders lower than the maximum value from the TRFL trace. With such low density, the contribution of singlet exciton to TA data is very low that is below the resolution of the measurement.