

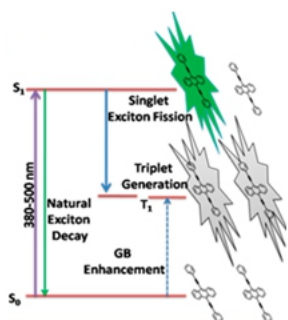
एकल विखंडन पदार्थ

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एकल विखंडन पदार्थ की पराद्रुत स्पेक्ट्रमिकी: जैविक प्रकाश-वोल्टिक में संभावनाएँ

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कार्बनिक अर्धचालक में एकल विखंडन

सारांश

एकल विखंडन (एस. एफ.), कार्बनिक पदार्थों में एक स्पिन अनुमत प्रक्रिया है जो एकल ऐक्साइटॉन को तीन गुना के जोड़े में खंडित करती है तथा संभावित रूप से शॉकले-क्विस्सर सीमा से परे कार्बनिक फोटोवोल्टिक उपकरण दक्षता में सुधार कर सकती है। हालांकि, ऊर्जावान और गतिकी बाधाओं के कारण, एसएफ केवल कुछ चुनिंदा कार्बनिक अणुओं तक ही सीमित है। मौजूदा और नए कार्बनिक पदार्थों में एसएफ प्रक्रिया को अनुकूलित करने के लिए एसएफ गतिकी का स्पेक्ट्रमिकी मूल्यांकन और संरचना-गतिकी संबंध को समझना अनिवार्य है। इस लेख में, हमने कार्बनिक अर्धचालक पदार्थों की पॉलीसीन श्रृंखला में एकल विखंडन के प्रकाश भौतिकी और पराद्रुत गतिकी का वर्णन किया है। एसएफ प्रक्रिया की स्पेक्ट्रमिकी पहचान, एसएफ गतिकी के संरचनात्मक तथा आकृति विज्ञान ट्युनिंग के महत्व और प्रकाश-वोल्टिक उपकरणों में इन पदार्थों के उपयोग के संभावित दायरे पर चर्चा की गई है।

मुख्य शब्द: कार्बनिक प्रकाश-वोल्टिक्स, एकल विखंडन, तीन गुना ऐक्साइटॉन, पराद्रुत स्पेक्ट्रमिकी

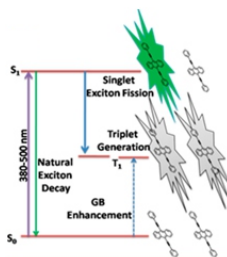
Singlet Fission Materials

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Ultrafast Spectroscopy of Singlet Fission Materials: Prospects in Organic Photovoltaics

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Singlet Fission in Organic Semiconductor

ABSTRACT

Singlet fission (SF), a spin allowed process in organic materials splits singlet exciton into a pair of triplets which can potentially improve organic photovoltaic device efficiency beyond Shockley-Quisser limit. However, due to energetic and kinetic constraints, SF is restricted to only a few selected class of organic molecules. Spectroscopic assessment of SF kinetics and understanding the structure-dynamics relation is imperative to optimize SF process in existing and new organic materials. In this article, we provide an overview of photophysics and ultrafast dynamics of singlet fission in polyacene series of organic semiconducting materials. Spectroscopic identification of SF process, importance of structural and morphological tuning of SF dynamics and potential scope of utilization of these materials in photovoltaic devices has been discussed.

KEYWORDS: Organic photovoltaics, Singlet fission, Triplet excitons, Ultrafast spectroscopy

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Introduction

Photovoltaics (PV), the direct solar-to-electrical conversion route is the backbone of renewable and sustainable energy resources. While silicon based solar cell is currently dominating the photovoltaic industry, development of cheaper and more efficient solar-electricity devices, such as organic photovoltaics, has been a persistent quest. Though organic semiconductor based PV systems has not reached competitive efficiency and long term stability as compared to silicon solar cells; lower cost, tunability, flexibility and foldable architecture has attracted great deal of research interest in organic photovoltaics (OPV). In the context of OPV, singlet fission (SF) has come up as a golden opportunity to cross the Shockley-Quisser (S-Q) efficiency limit [1]. In a single junction solar cell, theoretical efficiency is limited to about 33% of incident solar energy due to several loss factors; thermalization loss of above-band gap-energy being one of the dominant contributor (Fig.1). SF converts a singlet exciton to a pair of triplets by an efficient spin allowed mechanism, which can produce two charge-carriers per absorbed photon providing a potential route to increase organic photovoltaics efficiency. If fully exploited,

theoretical efficiency of singlet fission sensitized PV device can reach up to 45%. This prospect has attracted a great deal of research interest on SF photophysics in past one decade.

In singlet fission, singlet exciton energy is redistributed to generate a pair of triplet excitons. Thus, a potentially good SF molecule must satisfy thermodynamic criterion of $E(S_1) \geq 2E(T_1)$ [2]. Unlike intersystem crossing (ISC), SF being a spin allowed process, can proceed at fast enough rate to outcompete other de-excitation channels. However, SF requires spin exchange and sharing of singlet energy which introduce the requirement of strong intermolecular coupling to facilitate SF in ultrafast timescale. Requirement of isoergic or exoergic condition restricts SF process to be limited to a class of organic molecules, such as polyacenes (Fig.2). In addition, strong electronic coupling necessitates favorable intermolecular interaction in the solid state and kinetics of SF process is very much susceptible to crystal structure, sample morphology, defects and presence of polymorphs. Femtosecond resolved transient pump-probe spectroscopic measurement is imperative to assess the rate of SF vs other relaxation channels and to quantify the yield of triplets generated by SF route.

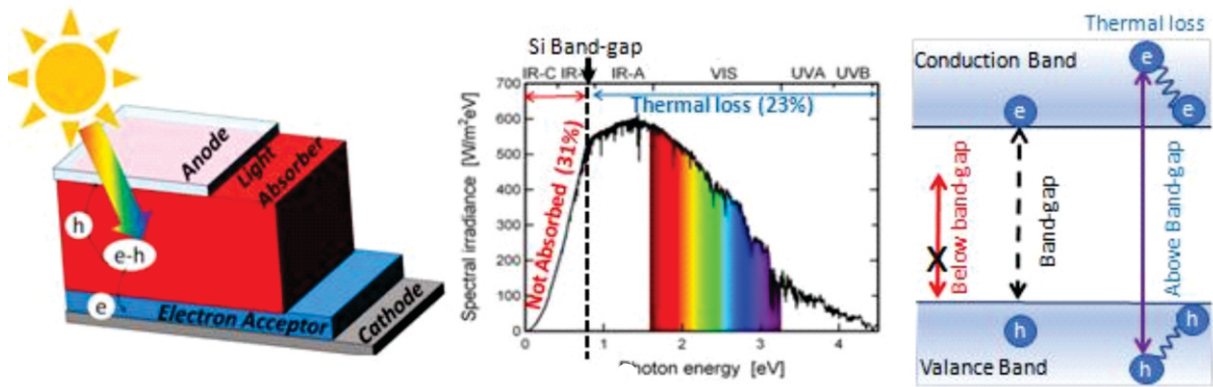


Fig.1: Schematic of single junction solar cell and energy loss mechanism due thermal loss of above band gap photon energy and no absorption of below band gap photon energy limiting theoretical efficiency to about 33%.

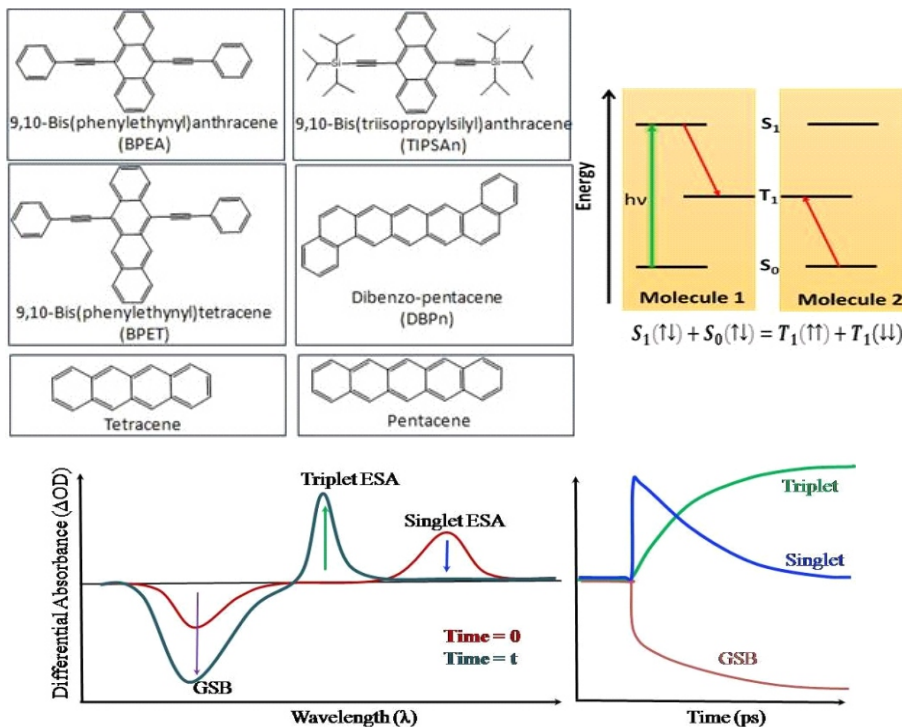


Fig.2: Molecular structure of a few representative polyacene based SF molecules and energy sharing diagram of singlet exciton to a pair of triplet excitons. Typical transient spectroscopic signature in SF process is illustrated.

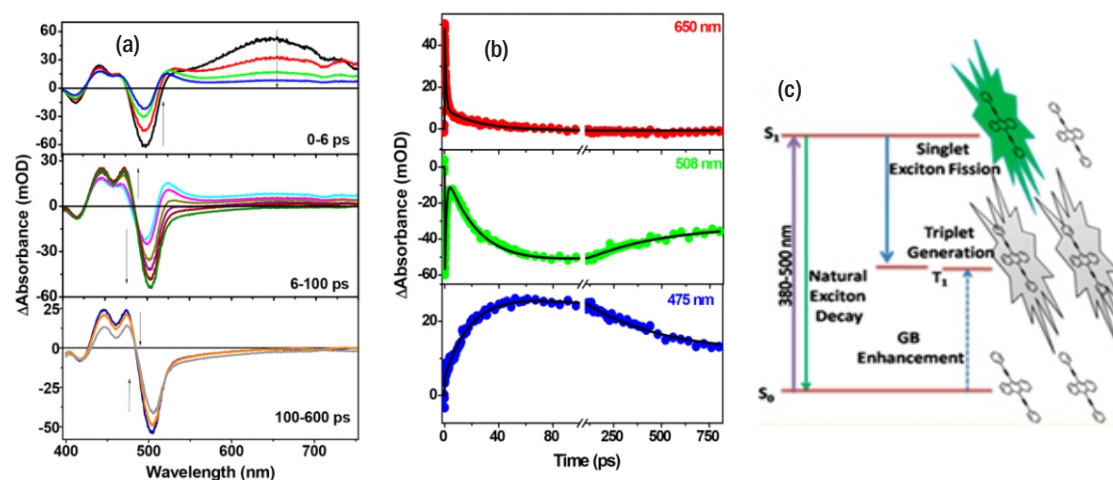


Fig.3: (a) Transient absorption spectral evolution of BPEA NA following singlet excitation by 390 nm 100 fs laser pulse. (b) Temporal kinetic profiles along with fitted data recorded at important wavelengths. (c) Schematic of transition associated with singlet fission process in BPEA. Adapted with permission from *J. Phys. Chem. C*, 122, (2018): 21047–21055.

Observation of excited state absorption (ESA) decay of singlet exciton, rise of triplet exciton ESA and concomitant rise in ground state bleach (GSB) signal is hallmark of SF process (Fig.2). In this article, we present ultrafast spectroscopic evaluation of SF dynamics in a few polyacene class of molecules (Fig.2) with an emphasis of structure and morphology dependence of SF rate and SF yield.

Singlet Fission in 9,10-bis (Phenylethynyl) Anthracene (BPEA): Our First Case Study

Due to endothermicity, anthracene is known to be an inefficient SF material. However, incorporation of phenylethynyl substitution in 9 and 10 position meets thermodynamic criterion of SF and is experimentally shown to facilitate fast SF with high yield [3]. Detailed photophysical and time resolved spectroscopic studies adopted to discern SF chemistry in BPEA nanoaggregate (NA) is described as follows. BPEA nanoaggregate prepared by flash precipitation in aqueous media display strongly perturbed absorption as compared to monomer suggesting strong intermolecular interaction in NA. On the other hand, strong quenching of emission (> 50 times) and fast decay of single exciton states in NA served as preliminary hint of SF process. To confirm fast deactivation pathway of singlet exciton, ultrafast pump-probe transient absorption spectroscopic studies were conducted. Transient absorption data (Fig.3) of BPEA NA shows broad singlet excited state absorption (ESA) at 650 nm region and ground state bleach (GSB) at 500 nm region. In very early timescale, fast decay of both ESA and GSB is due to singlet

exciton-exciton annihilation due to fast exciton diffusion. In later time, we observed rise of ESA at 475 nm corresponding to triplets of BPEA and rise of bleach at 520 nm.

Rise of bleach helped us to identify SF mechanism in this molecule for the first time. Quantitative estimation yielded triplet formation of 140-160% (depending on sample morphology) which corresponds to SF yield of 70-80% (Triplet yield = 2 x SF yield). Long lived nature of the triplets generated from SF process was verified from nanosecond transient absorption spectroscopy which showed SF generated triplet excitons of BPEA lived for more than 32 μs.

Effect of Bulky Substituent

Molecular structural modification can alter the energetics and molecular packing, incurring significant effect on SF yield. To exemplify influence of molecular packing on SF process, phenyl groups of BPEA was replaced by bulky isopropylsilyl group in 9, 10-Bis [(triisopropylsilyl) ethynyl] anthracene (TIPSA_n). This molecular structural change imparted negligible absorption shift and emission quenching in TIPSA_n, rather a red shifted broad emission from long lived excimer state is identified [4]. Notably, triplet yield found to be very low (<20%) which suggests inhibition of SF process and dominance of excimer state relaxation in TIPSA_n. Absence of SF in TIPSA_n is attributed to weak intermolecular interaction due to bulky substituent which does not provide necessary electronic coupling required for ultrafast SF. Thus molecular structure and consequent intermolecular packing in solid state plays a critical role in SF dynamics in polyacenes.

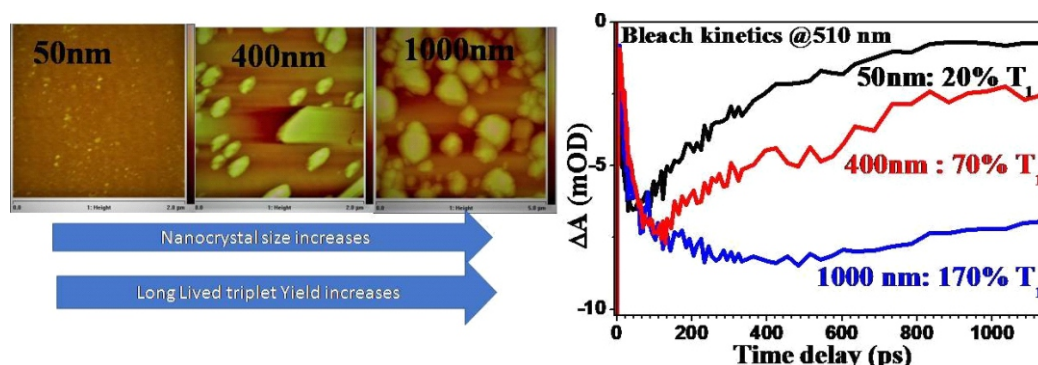


Fig.4: AFM image and bleach recovery kinetics of different sized nanocrystals of BPEA. As particle size increases, yield of long-lived triplets increases.

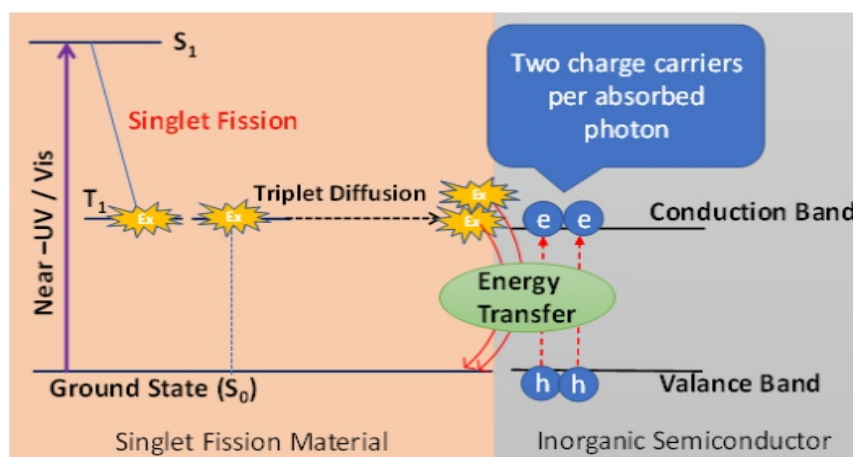


Fig.5: Proposed scheme of harvesting SF generated triplets in photovoltaics.

Importance of Extended Conjugation

While TIPSAn does not offer favourable packing for SF process, other structural modification on BPEA was explored by incorporating additional fused benzene ring. This extended conjugated derivative of BPEA, abbreviated as BPET (Fig.2) is shown to enhance SF yield [5]. Thin-film of BPET displays strong red shift of absorption band covering solar spectrum up to 650 nm and exhibits several orders of magnitude of emission quenching. Femtosecond pump-probe spectroscopy quantified SF yield of 90% (triplet yield=180%) occurring within a few picosecond timescale. Detailed analysis of transient absorption data led us to propose ultrafast triplet pair formation (< 200 fs) followed by separation into free triplets with a time constant of 1.4 ps.

Influence of Energetics

Longer π -conjugation in polyacenes is generally expected to impart faster SF kinetics due to stabilization of triplet states over singlet, resulting favorable thermodynamic driving force. However, when the conjugation length is moved beyond pentacene, additional factors come into picture. In pentacene, SF process is exothermic by ~ 0.12 eV and proceeds with rate constant of 80 fs, making it the fastest known SF material [6]. Extending conjugation beyond pentacene, such as hexacene and heptacene, SF rate is reported to slow down. In a nonlinearly fused heptacene (DBPn) derivative, we established that exothermicity exceeds 1 eV and SF process occurs with a time constant of 5.2 ps, more than 50 times slower than in pentacene [7]. Highly exothermic SF in DBPn requires multiphonon relaxation to dissipate excess energy released in SF process, resulting in slower SF rate. Thus, excessive exothermicity is shown to be detrimental for fast SF process.

Role of Sample Morphology

While ultrafast rate of SF is prerequisite of a good SF material to outcompete other nonradiative decay channels of singlet exciton, SF generated triplet excitons need to live long to convert them into charge-carriers. However, SF generated triplet excitons may undergo triplet-triplet annihilation and can disappear before energy extraction. Sample morphology is shown to play important role dictating fate of triplet excitons in BPEA nanoaggregate and thin film (Fig.4). While ultrafast singlet exciton fission kinetics is measured to be independent of particle size, SF generated triplet lifetime is shown to decrease with decrease in particle size. Transient absorption kinetics of small particles shows growth in bleach band up to 40 ps due to fast SF but subsequent ground state bleach

recovery in hundreds of ps highlights recombination of triplets before they separate into free triplets (Fig.4). Only a small fraction of signal (about 20%) survives beyond 1 ns which corresponds to free triplets. As particle size increases to several hundred nanometers, long-lived triplet yield increases to 70%. On the other hand, larger domain size in thin film exhibits almost negligible bleach recovery up to ns time scale with a triplet yield of 170%. Thus yield of free triplets is shown to be strongly dependent on particle size due to sample morphology dependent triplet separation kinetics.

Summary and Outlook

In summary, spectroscopy and ultrafast dynamics of singlet fission in polyacene class of molecules have been thoroughly investigated. We have described methodology of characterization SF process and different factors influencing the SF rate and yield. Ultrafast spectroscopic analysis on a series of polyacene derivatives led us to understand role of molecular structure and intermolecular interaction on SF process. Our study identified a first ever anthracene derivative with strong blue light absorption and high SF yield. Nanocrystal size and sample morphology is shown to play important role in SF dynamics. Structural tuning of thermodynamic and kinetics parameters of SF process in polyacenes have been thoroughly assessed. Systematic analysis of nanocrystal and thin film samples prepared under varied condition led us to optimize SF yield close to desirable value of 100%.

While high SF yield is demonstrated in many organic materials, the basic challenge associated with SF induced triplet exciton harvesting is finding suitable acceptor materials. Exploration of different semiconductor quantum dots as triplet harvester is necessary to find best acceptor material for SF sensitization (Fig.5). Diversity in synthetic methodology to add functionalities on existing SF chromophores is also required, not only to control SF energetic and electronic coupling (by crystal packing engineering) but also imparting required chemical stability and solution processibility. It is also important to note that apart from photovoltaics, SF generated triplet excitons may be leveraged to generate reactive singlet oxygen for photodynamic therapy or in other light harvesting methods such as photocatalysis.

Acknowledgment

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