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High-Lying 3¹A_q Dark-State-Mediated Singlet Fission

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Cite This: J. An	n. Chem. Soc. 2021, 143, 5691–569	97	Read Online		
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ABSTRACT: Singlet fission (SF), the conversion of one high-energy singlet to two low-energy triplets, provides the potential to increase the efficiency of photovoltaic devices. In the SF chromophores with C_{2h} symmetry, exemplified by polyenes, singlet-to-triplet conversion generally involves a low-lying $2^{1}A_{g}$ dark state, which serves as either a multiexciton (ME) intermediate to promote the SF process or a parasitic trap state to shunt excited-state populations via internal conversion. This controversial behavior calls for a deep understanding of dark-state-related photophysics involving the higher-lying singlet state. However, the optical "dark" and "transient" nature of these dark states and strong correlation feature of double exciton species make their characterization and interpretation



challenging from both experimental and computational perspectives. In the present work combining transient spectroscopy and multireference electronic structure calculations (XDW-CASPT2), we addressed a new photophysical model, i.e., a high-lying $3^{1}A_{g}$ dark-state-mediated ultrafast SF process in the benzodipyrrolidone (BDPP) skeleton. Such a $3^{1}A_{g}$ dark state with distinctive double excitation character, described as the ME state, could be populated from the initial $1^{1}B_{u}$ bright state on an ultrafast time scale given the quasi-degeneracy and intersection of the two electronic states. Furthermore, the suitable optical band gap and triplet energy, high triplet yield, and excellent photostability render BDPP a promising SF candidate for photovoltaic devices. These results not only enrich the arsenal of SF materials but also shed new insights into the understanding of dark-state-related photophysics, which could promote the development of new SF-active materials.

INTRODUCTION

Singlet fission (SF) has attracted ever increasing attention in the past decade due to its potential to overcome the Shockley– Queisser efficiency limit on single-junction solar cells.^{1–6} Although tremendous effort and progress have been made with newly developed SF-active materials,^{7–19} the most used SF materials in practical devices remain the archetype acenes, especially tetracene and pentacene, while implementation of SF in organic photovoltaic devices remains a formidable task.^{2,3,6} Therefore, the exploration of new design principles aiming at developing a broader library of SF chromophores is highly desirable.

Many SF chromophores with C_{2h} symmetry, such as polyenes, have a $1^{1}A_{g}$ ground state.¹ It has been theoretically predicted that a low-lying singlet excited state with the same A_{g} symmetry (labeled as $2^{1}A_{g}$) is needed for driving fission in either an intramolecular or intermolecular manner.^{1,20–22} For example, the lowest singlet excited state $(2^{1}A_{g})$ in polyene-type materials has been considered as a covalent state with multiexciton (ME) character that mediates the intramolecular singlet fission (iSF) process.^{23–28} However, the exact role that it plays still remains debatable.^{1,20,21} Gradinaru et al. first observed singlet transformation into the triplet on an ultrafast time scale in carotenoids bound to photosynthetic antenna.²⁶ Recent studies on iSF in a small molecule, quinoidal bithiophene, showed that the lowest 2¹A_g singlet state is a ME state.²⁹ However, Musser et al. demonstrated that iSF took place in solution of the conjugated polymer of poly(3dodecylthienylenevinylene) when excitation was at a photon energy above the bandgap, which is distinct to the case under band-edge excitation, in which no triplet generation can be observed.³⁰ Busby et al. also suggested that in the iSF-capable PBTDOn system excitation into the 1¹B_u state quickly converts internally to the 2¹A_g state and then to the ground state.¹⁷ This implies the dark $2^{1}A_{g}$ state acts as a parasitic trap state and shunts the excited-state populations via detrimental internal conversion (IC) (Scheme 1, left panel). Therefore, a deep investigation of dark-state-related photophysics is an urgent issue to develop efficient SF materials to take full advantage of this doubled triplet generation. However, the spectroscopic "dark" and "transient" nature of these dark states and strong correlation feature of ME species make the characterization and interpretation highly challenging from both experimental

Received: November 6, 2020 Published: April 12, 2021





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Scheme 1. Previous View and Proposed Model of Dark-State-Related Excited-State Photophysics



and computational perspectives.^{1,17,20–32} In the present work, combining multireference calculations and transient spectroscopy, we put forward a new photophysical model involving a higher lying state of $3^{1}A_{g}$ (Scheme 1, right panel). We show that this high-lying dark state, quasi-degeneracy in energy with the bright $1^{1}B_{u}$ state, could be populated from the latter via conical intersection between these two neighboring electronic states. During the preparation of this paper, Valentine et al. presented a theoretical work regarding higher-energy tripletpair states in polyenes and their role in the iSF process.³³ We demonstrated this by presenting a new SF chromophore of benzodipyrrolidone (BDPP) (Figure 1). Such a skeleton is



Figure 1. Chemical structure and steady-state absorption spectra of BDPP in dilute solution (black) and thin film (red).

equipped with strong blue-green light absorption, suitable triplet energy of 1.1-1.2 eV, high triplet yield of ~180%, and excellent photostability, rendering it a robust SF candidate for practical photovoltaic application.

EXPERIMENTAL SECTION

Materials and Sample Preparation. The BDPP molecule was synthesized according to previously reported routes with some modifications.³⁴ Thin films were prepared by a vacuum deposition technique on a sapphire or quartz substrate at a rate of 0.3 Å/s under a vacuum of 1×10^{-5} mbar.

Computational Methods. All geometry optimizations and reported energies are calculated using the XDW-CASPT2 method with the OpenMolcas package.^{35–38} The alkyl groups are omitted to simplify the model and reduce the computational costs (see section 7 of the Supporting Information for computational details).

Spectroscopic Measurements. All the spectra were measured at room temperature unless otherwise noted. UV-visible absorption and fluorescence spectra were measured on a Shimadzu UV-3600 spectrometer and Hitachi F-4500 spectrophotometer, respectively. A femtosecond laser system (Pharos, Light Conversion) delivered laser pulses at 1030 nm (180 fs, 6 kHz), which were then divided into two components by using a 9:1 beam splitter. The major component was sent to an optical parametric amplifier (Orpheus, Light Conversion) to generate the pump pulses (420 nm, 6 kHz). The minor component was further attenuated and focused into a 3 mm sapphire plate to generate the probe pulses. Both the pump and probe pulses were guided into a Harppia spectrometer, where time-resolved spectral data were recorded. A short-pass filter was inserted into the probe beam to cut off the fundamental light of 1030 nm. The time delay between the pump and probe beams was regulated through a computer-controlled motorized translation stage in the probe beam. The temporal resolution between the pump and the probe pulses was determined to be ~ 200 fs (fwhm). The transmitted light was detected by a CMOS linear image sensor. Species-associated kinetic analyses of fs-TA data were performed using singular value decomposition (SVD) followed by global fitting performed using lab-written MATLAB programs. A commercial nanosecond laser flash photolysis spectrometer (LP980-KS, Edinburgh) was used to perform ns-TA experiments. The pump laser pulse was obtained either from the third-harmonics generation Nd:YAG laser (Quanta-Ray LAB190, Spectra-Physics) at 355 nm or from an optical parametric oscillator (PrimoScan ULD400, Spectra-Physics) at 520 nm with a fwhm of no more than 10 ns. The probe light was provided by a 150 W pulsed xenon arc lamp. The transmission probe light was measured either by a single PMT detector (Hamamatsu R928) using a Tektronix model MDO3052 (100 MHz, 1.25 GS s^{-1}) digital oscilloscope at a specified wavelength for kinetic analysis or by an ICCD camera (DH320T, Andor) for spectral analysis. Analysis of the kinetic traces derived from time-resolved spectra was performed individually and globally using nonlinear least-squares fitting to a general sum-of-exponentials function after deconvolution of the instrument response function (IRF).



Figure 2. Energy diagram for the involved electronic states and the characteristics of the multiexciton state. (a) Energy diagram of involved excited states. (b) Canonical (left) and localized (right) molecular orbitals (CMOs and LMOs). (c) Linearly interpolated internal coordinate (LIIC) path connecting the $1^{1}B_{\mu}$ and $3^{1}A_{\mu}$ minima.

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Tabl	le 1	. Summaries	of	Excited-State	Energy	Diagram a	and Propeties	of the	BDPP	Skeleton
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symmetry	assignment	orbitals	configuration ^a	weight	vertical ^b	adiabatic ^c
2 ¹ A _g (dark)	S ₁	$H \rightarrow L$	(2ud0)	0.80	1.59	1.36
$1^{1}B_{u}$ (bright)	S ₂	$\text{H-1} \rightarrow \text{L}$	(u2d0)	0.29	2.89	$2.63(2.41^d)$
		$H-1/H \rightarrow L$	(ud20)	0.30		
		$\text{H-1} \rightarrow \text{L} + 1$	(u22d)	0.17		
3 ¹ A _g (dark)	ME	$H \rightarrow L$	(2020)	0.69	3.53	2.61
		LMOs	(udud)	0.31		
$1^{3}B_{u}$ (dark)	T_1	$\text{H-1} \rightarrow \text{L}$	(u2u0)	0.80		$1.20(\sim 1.1^d)$

^{*a*}Electronic configuration describes the occupation of the four electrons in the four molecular orbitals, written as (H-1, H, L, and L + 1), in which 2: occupied by two electrons, u: single electron with "up" spin, d: single electron with "down" spin, 0: empty (see Table S1 for electronic configuration in 12 electrons in 10 molecular orbitals representation). ^{*b*}Vertical excitation energy calculated at the FC region. ^{*c*}Adiabatic excitation energy calculated at the energy-minima structures (eV). ^{*d*}Experimental value of S₂ and T₁ states obtained from the absorption edge and triplet sensitization method, respectively (eV).

RESULTS AND DISCUSSION

Structure and Steady-State Characterization. The BDPP skeleton, ^{34,39,40} composed of the fused quinodimethane core and lactam rings with a distinctive C_{2h} symmetry (Figure 1), could be an ideal object to study dark-state-related photophysics given the lowest singlet excited state (S_1) is a symmetry-forbidden 2¹A_e dark state. UV-vis absorption spectra were recorded in dilute solution (concentration of 10^{-5} M) and vacuum-deposited thin films (Figure 1).³⁴ In *n*hexane, the spectrum presents an absorption maximum at 456 nm (2.72 eV) and an edge around 515 nm (2.41 eV), ascribed to the optically allowed transition of the S_0 (1¹ A_{σ}) $\rightarrow S_2$ (1¹ B_{μ}) state. The excitation energy to the $2^{1}B_{\mu}$ state is 3.08 eV, which is much higher than the absorption maxima by 0.36 eV and thus should play a negligible role under the present experimental conditions (for details, see section 7 of the Supporting Information). In the thin film, it shows an obvious absorption redshift with maxima at 495 nm, indicating strong intermolecular interactions. Furthermore, the molecule shows extremely low photoluminescence (PL) efficiency ($\Phi_{\rm F} < 0.01$) in both solution and thin film (Figure S4), implying that there are efficient nonradiative excited-state relaxation pathways.^{15,16} The triplet energy level, $E(T_1)$, was then determined using the triplet-triplet energy-transfer method (for details see section 6 of the Supporting Information).¹⁵ With $E(S_2) = 2.41$ eV and $E(T_1) = 1.1 - 1.2$ eV, the BDPP molecule fulfills the energetic criterion $E(S_2) \ge 2 \times E(T_1)$ for an efficient SF process, ascribed to the diradical character of such a quinoidal skeleton.41

Capture of the Multiexciton Dark State. Multireference XDW-CASPT2(12,10) calculations were carried out to study excited-state energy diagrams, especially obscure dark states and possible ME states (Figure 2).^{1,1,7,20-32,37} On the basis of the optimized ground-state (1^1A_g) structure, we explored the electronic structures of the relevant excited states, i.e., 11Ag $2^{1}A_{g}$, $1^{1}B_{u}$, and $3^{1}A_{g}$ singlet states as well as the first triplet $1^{3}B_{u}$ state (Figure 2, Table 1). The strongly allowed H-1 \rightarrow L singly excited transition leads to the optically bright S₂ 1¹B_u state, which represents the usual entry point into the excited singlet manifold by absorption of light. The lowest singlet state (S_1) is an actually symmetry-forbidden 21Ag dark state, but this state embodies $H \rightarrow L$ singly excited electronic transition rather than double-excitation character observed in pentacene and quinoidal bithiophene. 29,31,32 Surprisingly, the high-lying $3^1\mathrm{A_g}$ singlet state above the 1¹B_u state is another dark state and features double-excitation character, referred to as the ME $(3^{1}A_{\sigma})$ state. In this dark state, double excitation involves

simultaneous promotion of two electrons from occupied to unoccupied orbitals, specifically $H \rightarrow L$ transition with electronic configuration of (2020), which definitely indicates its ME character (Table 1).

To more clearly demonstrate the ME character of the wave function for this state, canonical molecular orbitals (CMOs) are linearly transformed into the localized molecular orbitals (LMOs).³¹ Results show that these LMOs are mainly positioned on the opposite sides of the BDPP skeleton (Figure 2b). Subsequent configuration interaction calculations show that the dominant configuration (udud) has one electron in each localized orbital and weight of 0.31 of the wave function (Table 1), which finally produces four unpaired electrons occupying the spatially localized orbitals. Therefore, this dark state can be described as two electron—hole pairs located on the opposite ends of the molecule, which turn out to be a triplet pair coupled into an overall singlet ME state.

We then explored the minimum-energy regions for the relevant excited states (Figures 2c and S8). Results indicate that the S₂ (1¹B_u), S₁ (2¹A_g), ME (3¹A_g), and T₁ (1³B_u) state minima are predicted to be 2.63, 1.36, 2.61, and 1.20 eV, respectively (Table 1). It is important to note that the energy ordering of the S_2 (1¹ B_u) and ME (3¹ A_o) states is inverted when passing away from the Franck-Condon region. The initial higher $3^{1}A_{\sigma}$ state becomes slightly lower than the $1^{1}B_{\mu}$ state, and two states are actually quasi-degenerate in energy (0.02 eV). Moreover, the computational results regarding the linearly interpolated internal coordinate (LIIC) pathway from the $1^{1}B_{u}$ to $3^{1}A_{g}$ ME state (Figure 2c) exhibit a crossing point between the two electronic states. Given the quasi-degeneracy and intersection of the two states, the $1^{1}B_{u} \rightarrow 3^{1}A_{g}$ process is generally accepted to occur on a time scale of subpicosecond or shorter and outperforms other radiative and nonradiative processes, possibly including the $1^{1}B_{u} \rightarrow 2^{1}A_{g}$ process. This is well consistent with the experimental results discussed below.

Ultrafast Multiexciton Formation in Solution. We performed femtosecond transient absorption (fs-TA) experiments for in-depth investigation of dark-state-related photophysics of the BDPP skeleton. In dilute solution, the spectra consist of clear ground-state bleaching (GSB) at 466 nm and an intense excited-state absorption (ESA) band at 810 nm assigned to the initially populated bright $1^{1}B_{u}$ S₂ state (Figure 3a). This ESA from $1^{1}B_{u}$ rises within IRF and decays rapidly in <1 ps (Figure 3b). Concurrent with the decay of this feature, new absorption bands appear around ~618 nm with a rising time of 0.92 ps, assigned to the $3^{1}A_{g}$ dark state. The matching between the decay of S₂-ESA at 810 nm and the rise of $3^{1}A_{g}$ -



Figure 3. Multiexciton formation in dilute solution. (a) fs-TA spectra and (b) corresponding kinetics for the BDPP molecule excited at 450 nm. (c, d) Species-associated spectra from the global fitting results based on a sequential two-state model. A sensitized triplet ESA curve is included in (c) to help triplet-like species assignment.

ESA at 618 nm suggests the quantitative conversion between these two transient species, which is supported by the ultrafast IC process of the $1^{1}B_{u} \rightarrow 3^{1}A_{g}$ state predicted theoretically (Figure 2c). Subsequently, ESA signals from the $3^{1}A_{g}$ state between 600 and 850 nm decay with a time constant of ~7 ps, which is in agreement with the monoexponential recovery of the corresponding GSB signal at 466 nm (7.2 ps, Figure 3b). There is no long-lived signal observed in the solution phase upon direct excitation.

Global analysis based on a sequential two-state model results in the lifetimes of 0.9 ps for $1^{1}B_{\mu}$ S₂ and 7.2 ps for the $3^{1}A_{\mu}$ state, respectively (Figure 3c and 3d). Figure 3c presents the species-associated spectra from the global fitting results along with a sensitized ESA curve of T_1 (1³B_u) in the solution (for details of triplet sensitization see Figure S6). The 3¹A_o stateassociated TA spectrum is comparable to the line shape of sensitized T_1 , suggesting that the former is a transient species with distinct triplet character. In combination with the above computational results, we preferentially assign this 3¹A_g state to the intramolecular ME state (the spectral discrepancy at 600 nm is observed between the assigned ME state and the sensitized triplets to the presence of strong intertriplet interaction). Solvent-dependence measurements indicate that such a ME state has some partial CT character, which is highly possible in the push-pull BDPP skeleton (for details see section 8 of the Supporting Information). Then this ME state rapidly decays to the ground state via triplet-triplet annihilation (TTA) rather than undergoing further dissociation due to strong intertriplet interaction (Figure 3d).^{21,22} These results confirm that a high-lying $3^1A_{\mathfrak{g}}$ ME state mediates the excited-state deactivation in dilute solution of the BDPP molecule.

Efficient Triplet-Pair Separation in Thin Films. Figure 4 presents fs-TA spectra and corresponding global analysis results for the BDPP thin film (100 nm). At the initial stage, it presents a spectral evolution similar to the case in dilute solution. That is, a rapid decay of S_2 -ESA around 830 nm is concurrent with a rise of the 3^1A_g state around 630-680 and 800 nm (Figures 4a and 4b), respectively. At longer time delays (>10 ps), following the decay of the 3^1A_g state, a new spectral species appears and seriously overlaps with the GSB



Figure 4. Triplet pair separation in thin films. (a) fs-TA spectra and (b) corresponding kinetics for BDPP thin film excited by 450 nm. (c) The comparison of TA spectra (delay times at 100 ps and 0.1 μ s) and the sensitized triplet ESA curve. (d) Species-associated spectra from the global fitting results based on a sequential four-state model.

signal around 500-600 nm. This species is confirmed to be long-lived triplets persisting to several microseconds by ns-TA measurements (Figure S15) and a triplet sensitization experiment^{9,15,42} (Figure S16, for details see section 12 of the Supporting Information). It can be seen from Figure 4c that the line shape of the sensitized T₁ state fits well with the TA curves at 100 ps and 0.1 μ s, indicating the end signals in TA measurements are definitly free triplets. We ruled out the possibility of charge transfer (CT)-like or charge separation states as the end species, given the lack of distinct characteristic absorption bands of these transient species around 400-500 and 800 nm.⁴⁰ The overall triplet yield (Φ_T) of BDPP thin films was estimated to be 179 \pm 20% using an energy-transfer method following the procedure reported previously (for details see section 13 of the Supporting Information). These results indicate that triplet formation definitely results from the SF channel, the only process by which more than one triplet can be generated from one photoexcitation-populated singlet exciton. As discussed above, the strong intertriplet interaction of the 3¹A_o ME state limits its further intramolecular dissociation into a pair of triplets; however, in solid films, this ME state prefers to evolve into an intermolecular $^{1}(TT)$ state from which two free triplets are eventually generated. Such intramolecular to intermolecular dissociation of the ME state in aggregates is facilitated by both molecular structural torsion and strong push-pull strength.^{21,22} This is as well supported by weak binding energy of intertriplets in a BDPP dimer model, as indicated by the calculated small energy difference between both intermolecular $^{1}(TT)$ and $^{5}(TT)$ states (0.1 eV, for details see Table S3 in section 7 of the Supporting Information). Therefore, we proposed that the intermolecular separation of the ME state is responsible for these long-lived triplets in solid aggregates.

The fs-TA data of thin films were best fit to a sequential four-state kinetic model with an intermediate $(1^{1}B_{u} \rightarrow 3^{1}A_{g} \rightarrow {}^{1}(TT) \rightarrow T_{1} \rightarrow S_{0}$, Figures 4d), despite attempts to fit the data to a simpler three-state model and a branched model in which $3^{1}A_{g}$ decay was a parallel process (for details of global analyses see section 14 of the Supporting Information). We acknowledge that film heterogeneity might result in defect sites or sites with different SF rates, which do not act as intermediates.⁹ In

our four-state model, the third species, as a key intermediate for triplet formation, has some features of both $3^{1}A_{\sigma}$ and free T_1 states and then is assigned to an intermolecular triplet-pair state, labled as $^{1}(TT)$. That is, after photoexcitation, the initial bright $1^{1}B_{u}(S_{2})$ state populates $3^{1}A_{g}$ via conical intersection at an ultrafast rate of 0.2 ps. Then the 3¹A_g state as a key ME intermediate can undergo an intramolecular to intermolecular evolution (1.7 ps) that occurs in adjacent BDPP molecules and loads the ¹(TT) state. Within $\tau = 22.6$ ps, the formed ¹(TT) can further decorrelate to dissociate into free triplets, which can persist over several microseconds. In the current system, the quasi-degeneracy and intersection of the 31Ag dark and 1¹B_u bright states result in an ultrafast and quantitative SF process that outperforms other radiative and nonradiative processes, such as to the excimer trap state^{31,43} and to the low-lying $2^{1}A_{g}$ dark state.^{17,30,44,45} In addition, CT and excimer-like states are frequently involved in SF systems.^{19,11,17,20,22} Mauck et al. presented that an excimer intermediate with distinct CT configurations can promote a fast SF process in diketopyrrolopyrrole (DPP), a similar molecule to the current BDPP system.⁹ Given the slightly broader absorption band of 3¹A_g in TA spectra of films relative to solution and the partial overlapping ESA bands of $3^{1}A_{g}$ or $^{1}(TT)$ with radical species, the $3^{1}A_{g}$ or $^{1}(TT)$ state might have partial CT or excimer character to mediate the fast SF process of the current system as observed in DPP derivatives.^{1,9,20,22}

Proposed Model for Dark-State-Related Photophysics. Based on the results of transient spectra and theoretical calculations, we proposed a new model for dark-state-related photophysics: a distinct high-lying dark-state-mediated SF process. As shown in Scheme 2, the ultrafast IC process from

Scheme 2. Proposed Model for the High-Lying Dark-State-Mediated SF Process



the initially populated 1^{1} Bu to $3^{1}A_{g}$ ME state occurs within 1 ps. Such an ultrafast excited-state event fails the sequential IC processes to the lower $2^{1}A_{g}$ and $1^{1}A_{g}$ states. However, the further separation of the $3^{1}A_{g}$ ME state is heavily suppressed in dilute solution because of the much stronger binding interaction of intertriplets. This is consistent with the calculated high-energy 5(TT) state, which is 1.5 eV more than the ME state within one BDPP molecule (for details see Table S1 in section 7 of the Supporting Information). Instead, the TTA process takes place. Differently, in solid films, the unimolecular 3¹A_g ME state could first evolve into an intermolecular $^1(\Tilde{T}T)$ state with a time costant of 1.7 ps. Due to the much smaller binding energy of intertriplets in the BDPP dimer, the $^{1}(TT)$ state can easily dissociate into two free triplets in aggregetes (22.6 ps). This is seconded by the calculated smaller energy difference between the intermolecular ${}^{1}(TT)$ and ${}^{5}(TT)$ states (0.1 eV, Table S3). These free

triplets have long-lived lifetimes at the μ s time scale. Besides 1 (TT), the high-spin triplet-pair 5 (TT) state is also involved in intermolecular SF dynamics.^{20–22,46–48} For instance, Guldi and co-workers recently explored the SF dynamics of carbenebased diradical dimers and found both ¹(TT) and ⁵(TT) are close to each other in energy because of the weak binding energy of intertriplets.⁴⁶ This is also consistent with the recent theoretical work by the Scholes group.⁴⁷ However, the further exploration on the role of ${}^{5}(TT)$ in SF dynamics of our studied system in solid films is beyond the scope of the present study and will be studied in the near future. Finally, Sandoval-Salinas and Casanova recently proposed a dark-state-mediated SF mechanism for a simple ethylene-dimer model in which the locally doubly excited HOMO-to-LUMO singlet state has a significant impact on SF dynamics at the eclipsed conformation.⁴⁸ However, this dark state is the lowest excited singlet state of an intermolecular SF system, which is different from our proposed higher-lying dark-state-mediated SF mechanism for intramolecular SF systems.

The proposed model highlights that the high-lying $3^{1}A_{\sigma}$ dark state serves as a key intermediate to promote efficient ME generation in solution and the triplet-separation process in solid films (Scheme 2). The quasi-degeneracy of the $3^{1}A_{\sigma}$ and $1^{1}B_{u}$ states renders the minimum energy loss from the bright state, while the low-lying 2¹A_g state acts as a potential IC channel competing with the SF process but is at a disadvantage relative to the latter. Therefore, such a high-lying dark-statemediated SF process not only features ultrafast and highly efficient merits of ME generation but also could reserve the absorbed photon energy to the maximum extent conducive to practical photovoltaic conversion.¹⁻³ Moreover, the results also indicate that more electronic states, not just $1^{1}B_{u}$ and $2^{1}A_{g}$ states, need to be taken into consideration to supply more realistic photophysics. The generality of this model is underway in our lab.

CONCLUSION

Combining transient spectroscopy and theoretical calculations, we provided a clear picture of the high-lying $3^{1}A_{\sigma}$ dark-statemediated efficient SF and subsequent triplet pair separation process in the benzodipyrrolidone skeleton. Such a dark state features distinctive double excitation character and could be described as the ME state composed of two strongly coupled triplet states. Moreover, this high-lying dark state, which is quasi-degenerate in energy with the $1^{1}B_{u}$ bright state, could be populated from the latter at an ultrafast rate via the intersection of two states. Furthermore, the reported SF system features strong absorption in the blue-green region, suitable triplet energy, an ultrafast and efficient SF process, and high resistance against air and light, which could provide great potential for integration into practical photovoltaic devices. Our work not only enriches the pool of SF materials and provides robust candidates for practical applications but also contributes new insights to dark-state-related photophysics, which could be widely applied to the development of new SFactive materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c11681.

Journal of the American Chemical Society

Data on synthetic and theoretical calculation details, triplet-state sensitization, spectral analysis, and triplet yield (PDF)

Accession Codes

CCDC 1904681 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant Nos. 22005210, 22090022, 21833005, 21790364, 21573251, 21688102, and 21590801), the National Key Research and Development Program of China 2017YFA0204503, the Beijing Natural Science Foundation of China (Grant No. 2162011), Project of State Key Laboratory on Integrated Optoelectronics of Jilin University (IOSKL2014KF16), and the Youth Innovative Research Team of Capital Normal University.

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