

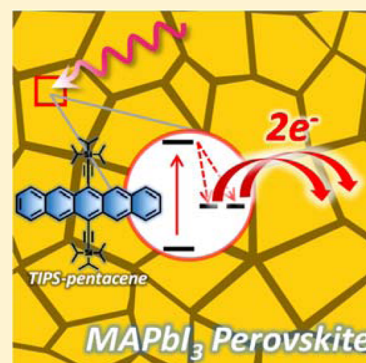
Electron Transfer from Triplet State of TIPS-Pentacene Generated by Singlet Fission Processes to $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite

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S Supporting Information

ABSTRACT: To reveal the applicability of singlet fission processes in perovskite solar cell, we investigated electron transfer from TIPS-pentacene to $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) perovskite in film phase. Through the observation of the shorter fluorescence lifetime in TIPS-pentacene/MAPbI₃ perovskite bilayer film (5 ns) compared with pristine MAPbI₃ perovskite film (20 ns), we verified electron-transfer processes between TIPS-pentacene and MAPbI₃ perovskite. Furthermore, the observation of singlet fission processes, a faster decay rate, TIPS-pentacene cations, and the analysis of kinetic profiles of the intensity ratio between 500 and 525 nm in the TA spectra of the TIPS-pentacene/MAPbI₃ perovskite bilayer film indicate that electron transfer occurs from triplet state of TIPS-pentacene generated by singlet fission processes to MAPbI₃ perovskite conduction band. We believe that our results can provide useful information on the design of solar cells sensitized by singlet fission processes and pave the way for new types of perovskite solar cells.



After singlet fission was first discovered in 1965 as a way to explain delayed fluorescence in anthracene crystals,¹ singlet fission research received much attention in an attempt to circumvent the Shockley–Queisser limit² in photovoltaic devices because each of the two triplet excitons generated by singlet fission processes can produce electrons after dissociation at the interface.^{3,4} Previous studies reported that the maximum theoretical thermodynamic efficiency of a single-junction solar cell is increased from 32 to 46% by singlet fission processes.^{5,6} Furthermore, Zhu et al. used time-resolved two-photon photoemission spectroscopy to show that multiple electron transfers occur from the two triplet states generated by singlet fission processes to fullerene.⁷ These results have ignited a desire for new types of light harvesting devices sensitized by singlet fission processes to increase the efficiency of solar cells. For this reason, many research groups have made strenuous efforts to find new materials exhibiting singlet fission processes.^{8–10} However, only a few examples of solar cells sensitized by singlet fission processes have been reported, and these include pentacene/fullerene bilayers,¹¹ pentacene/PbS,¹² pentacene/PbSe,¹³ pentacene/phthalocyanine/fullerene trilayers,¹⁴ and pentacene/PTCDI blends.¹⁵ Moreover, the conversion of high-energy singlets into pairs of low-energy triplets via singlet fission processes in light-harvesting devices does not generally yield a high power conversion efficiency because solar cell materials possess intrinsically low power conversion efficiencies.

To address this issue, we investigated electron-transfer dynamics between TIPS-pentacene as a singlet fission material and $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) perovskite nanocrystals as an electron acceptor material to reveal the applicability of singlet fission processes in the perovskite solar cell. The perovskite was first employed as sensitizer in TiO_2 dye-sensitized solar cell for

visible-light conversion.¹⁶ However, fabrication of perovskite photovoltaics was limited due to dissolution issue of perovskite in liquid electrolyte. The perovskite photovoltaics was triggered by the development of long-term stable solid-state perovskite solar cell,¹⁷ which have drawn considerable attention in recent years as promising materials that can be used to develop high-performance photovoltaic devices at a low cost.^{18–21} Moreover, their high absorption coefficient, tunable band gap, low-temperature processing, and abundant elemental constituents provide numerous advantages over most thin-film absorber materials. In addition, TIPS-pentacene has a high singlet fission yield^{22,23} and hole mobilities in the solid state.^{24,25} In particular, the optical energy state (conduction and trap bands) of MAPbI₃ perovskite nanocrystals (4.1 eV) is well-matched with the triplet state of TIPS-pentacene (4.0 eV).^{26,27} Therefore, it is relevant to investigate electron-transfer dynamics between TIPS-pentacene and MAPbI₃ perovskite because the target systems seem to be ideally suited for highly efficient solar cells sensitized by singlet fission processes.

We measured steady-state absorption spectra of TIPS-pentacene, MAPbI₃ perovskite, and TIPS-pentacene/MAPbI₃ perovskite bilayer films, which were fabricated by spin-casting at 5000 r.p.m (Figure 1). The absorption spectra of TIPS-pentacene and MAPbI₃ perovskite films are identical to previous results.^{28,29} Compared with the absorption spectrum of TIPS-pentacene solution, red-shifted and different transitions were observed in film phase, which is originated from the formation of 2D π -stacked structures.^{23,30} Moreover, the absorption spectrum of the TIPS-pentacene/MAPbI₃ perov-

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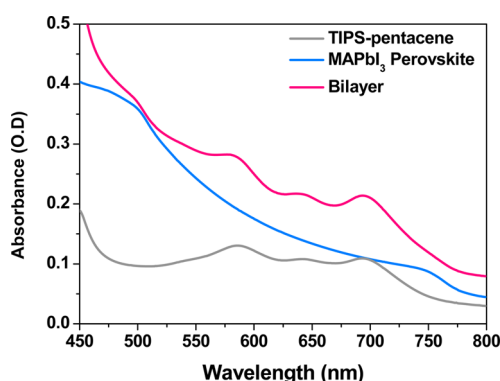


Figure 1. Steady-state absorption spectra of TIPS-pentacene (gray), MAPbI₃ perovskite (blue), and TIPS-pentacene/MAPbI₃ perovskite bilayer (red) films.

skite bilayer film was approximately the sum of the absorption spectra of TIPS-pentacene and MAPbI₃ perovskite films. In particular, the absorption bands at 585, 643, and 694 nm in TIPS-pentacene/MAPbI₃ perovskite bilayer film were consistent with those in TIPS-pentacene film, indicating that electronic interactions between TIPS-pentacene and MAPbI₃ perovskite are negligible. Although we could not find any features originating from interactions between TIPS-pentacene and MAPbI₃ perovskite in the absorption spectrum of TIPS-pentacene/MAPbI₃ perovskite bilayer film, the fluorescence lifetime of TIPS-pentacene/MAPbI₃ perovskite bilayer film (5.0 ns) was shorter than that of MAPbI₃ perovskite film (20 ns) (Figure S1 in the [Supporting Information](#)). This shorter fluorescence lifetime might be attributed to electron transfer between TIPS-pentacene and MAPbI₃ perovskite,³¹ which supports the fact that the efficiency of MAPbI₃ perovskite solar cell can be enhanced by electron transfer between TIPS-pentacene and MAPbI₃ perovskite.

To confirm that this electron transfer really originated from the triplet state of TIPS-pentacene generated by the singlet fission processes, we measured the femtosecond transient absorption (TA) spectra of TIPS-pentacene, MAPbI₃ perovskite, and TIPS-pentacene/MAPbI₃ perovskite bilayer films. The TA spectra were obtained using the same excitation power (450 μ W) in a homemade vacuum chamber (~ 0.0005 Torr) at room temperature. The TA spectra of the TIPS-pentacene film exhibited growth in an excited-state absorption band at 525 nm as the delay time increased (Figure 2a,c). This rise feature was fitted with a time constant of 1.1 ps. Because the excited-state absorption at 525 nm was assigned to the excited-state absorption of the triplet state of TIPS-pentacene and the time constant of the rise feature is well-matched with the previous result, we confirmed that this rise process was caused by an increase in the triplet excited-state population via the singlet fission processes of TIPS-pentacene.²³ In the case of the TIPS-pentacene/MAPbI₃ perovskite bilayer film, we also detected a fast rise component at 525 nm with a time constant of 1.1 ps, which is consistent with the case of the TIPS-pentacene film (Figure 2b,c). Because no such fast rise dynamics except for the band filling effect in the bleaching region²⁹ was observed in the excited-state absorption of the MAPbI₃ perovskite film (Figure S2 in the [Supporting Information](#)), we confirmed that the singlet fission processes of TIPS-pentacene occurred in the TIPS-pentacene/MAPbI₃ perovskite bilayer film upon photoexcitation. Recently, Wasielewski et al. reported that the rise feature of excited-

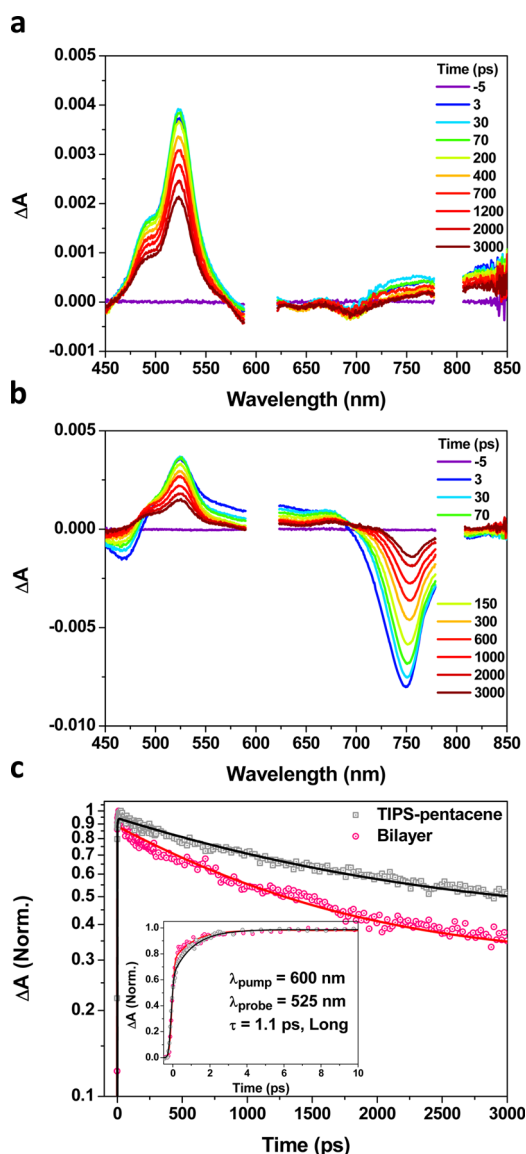


Figure 2. TA spectra of (a) TIPS-pentacene and (b) TIPS-pentacene/MAPbI₃ perovskite bilayer films upon photoexcitation at 600 nm. (c) Normalized decay profiles of TIPS-pentacene (gray) and TIPS-pentacene/MAPbI₃ perovskite bilayer (red) films. Inset: The decay profiles over a short time interval.

state absorption disappears for a TIPS-pentacene:PDI blend film because the singlet fission processes of TIPS-pentacene are inhibited by electron transfer from the singlet state of TIPS-pentacene to PDI derivatives.²³ This previous study indicates that the singlet fission processes are restricted through the formation of TIPS-pentacene cations by electron transfer in the singlet excited-state. Accordingly, the existence of singlet fission processes in TIPS-pentacene/MAPbI₃ perovskite bilayer film can be an indirect evidence that electron transfer in singlet state of TIPS-pentacene is negligible. Additionally, we observed different lifetimes when monitoring TIPS-pentacene and TIPS-pentacene/MAPbI₃ perovskite bilayer films at 525 nm (Figure 2c). Although both TIPS-pentacene and TIPS-pentacene/MAPbI₃ perovskite bilayer films exhibited similar spectral features corresponding to singlet fission processes at 525 nm, the decay rate for the TIPS-pentacene/MAPbI₃ perovskite bilayer film was faster than that for the TIPS-pentacene film. Because the excited-state absorption of MAPbI₃ perovskite at

525 nm was negligible, the faster decay rate in the TIPS-pentacene/MAPbI₃ perovskite bilayer film indicates the existence of additional electron transfer dynamics after the singlet fission processes. Furthermore, the ratio of fast rise components is almost the same in the normalized decay profiles of TIPS-pentacene and TIPS-pentacene/MAPbI₃ perovskite bilayer films, which supports the idea that electron transfer from the singlet excited-state of TIPS-pentacene to MAPbI₃ perovskite can be negligible (Inset in Figure 2c). Therefore, these observations imply that electron transfer occurs in the triplet state of TIPS-pentacene, which was further supported by the observation of additional spectral features in TIPS-pentacene/MAPbI₃ perovskite bilayer film compared with those in TIPS-pentacene and MAPbI₃ perovskite films.

Previous studies reported that the TIPS-pentacene cation peak in the film phase is located at ~ 500 nm, which is different from the case of solution phase.³² However, it is difficult to directly observe the TIPS-pentacene cation peak because the excited-state absorption of TIPS-pentacene and the ground state bleaching of MAPbI₃ perovskite are included in the TA spectra of TIPS-pentacene/MAPbI₃ perovskite bilayer film at 500 nm. Accordingly, we subtracted the TA spectra of TIPS-pentacene and MAPbI₃ perovskite films from those of the TIPS-pentacene/MAPbI₃ perovskite bilayer film to reveal the TIPS-pentacene cation peak (Figure 3a and Figure S3 in the Supporting Information).³³ In the subtracted TA spectra of the TIPS-pentacene/MAPbI₃ perovskite bilayer film, we observed

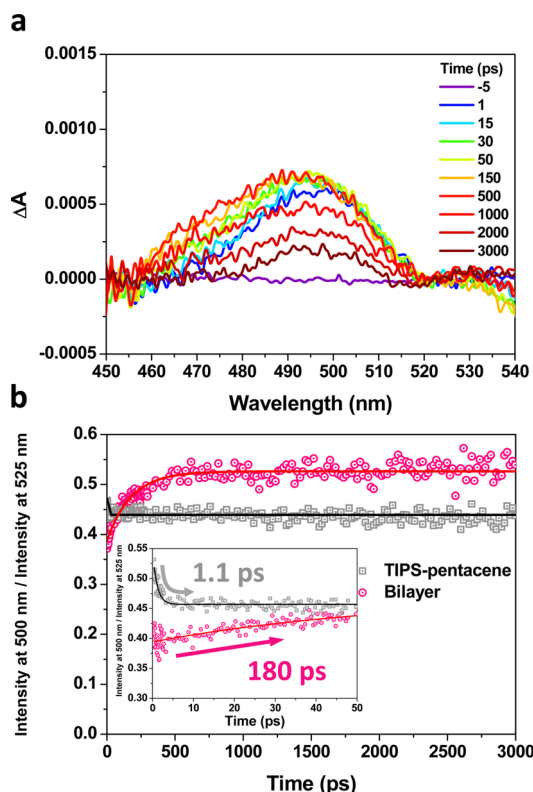


Figure 3. (a) Subtracted TA spectra of TIPS-pentacene/MAPbI₃ perovskite bilayer film. TA spectra of TIPS-pentacene and MAPbI₃ perovskite films were subtracted from those of TIPS-pentacene/MAPbI₃ perovskite bilayer film. (b) Kinetic profiles of intensity ratios between 500 and 525 nm in TIPS-pentacene (gray) and TIPS-pentacene/MAPbI₃ perovskite bilayer (red) films. Inset: The peak ratios over a short time interval.

additional excited-state absorption at 495 nm, which is well-matched with previously reported TIPS-pentacene cation peak in the film phase. Therefore, we confirmed electron transfer from TIPS-pentacene to MAPbI₃ perovskite in TIPS-pentacene/MAPbI₃ perovskite bilayer film. Additionally, we investigated the intensity ratio (I at 500 nm/ I at 525 nm) in the region between 500 and 525 nm to verify that the TIPS-pentacene cation was generated by the triplet state of TIPS-pentacene in the TIPS-pentacene/MAPbI₃ perovskite bilayer film (Figure 3b). In the case of the TIPS-pentacene film, we observed a consistent intensity ratio after a fast decay with a time constant of 1.1 ps originated from the singlet fission processes of TIPS-pentacene. However, the intensity ratio of TIPS-pentacene/MAPbI₃ perovskite bilayer film exhibited different kinetic profiles. Because the TA signal of the TIPS-pentacene/MAPbI₃ perovskite bilayer film at 500 nm was largely mixed with the negative bleaching signal of MAPbI₃ perovskite, the intensity ratio of the TIPS-pentacene/MAPbI₃ perovskite bilayer film should have been smaller than that of the TIPS-pentacene film. Although the intensity ratio of the TIPS-pentacene/MAPbI₃ perovskite bilayer film was smaller than that of the TIPS-pentacene film over a short time interval, we observed that the intensity ratio of the TIPS-pentacene/MAPbI₃ perovskite bilayer film became larger than that of TIPS-pentacene as the delay time increased. If the rise dynamics of the intensity ratio of the TIPS-pentacene/MAPbI₃ perovskite bilayer film could only be attributed to the recovery of the negative bleaching signal of MAPbI₃ perovskite, then the intensity ratio of the TIPS-pentacene/MAPbI₃ perovskite bilayer film should be identical to that of a TIPS-pentacene film over longer time interval. In contrast, we observed a larger intensity ratio for the TIPS-pentacene/MAPbI₃ perovskite bilayer film, indicating an existence of additional excited-state absorption at 500 nm. Furthermore, the rate of this rise kinetics was too slow to be caused by cations generated directly from the singlet excited-state of TIPS-pentacene.³⁴ On the basis of these spectroscopic and kinetic results, we concluded that electron transfer occurs from the two triplet states of TIPS-pentacene generated by singlet fission processes to MAPbI₃ perovskite.

The electron-transfer dynamics in a TIPS-pentacene/MAPbI₃ perovskite bilayer film is presented in Figure 4.

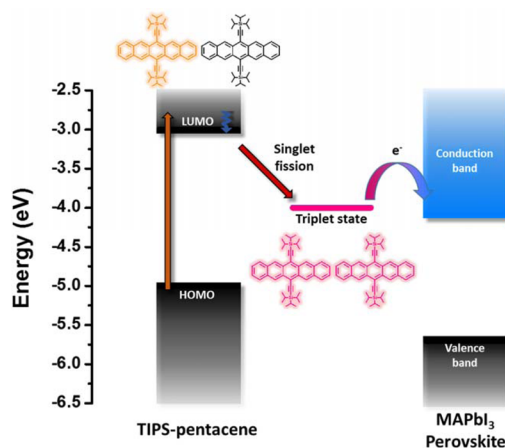


Figure 4. Schematic diagram of the electron-transfer dynamics from TIPS-pentacene to MAPbI₃ perovskite in a TIPS-pentacene/MAPbI₃ perovskite bilayer film.

Upon photoexcitation of TIPS-pentacene, the singlet fission processes occur with a time constant of 1.1 ps. As a result of the singlet fission processes of TIPS-pentacene, the excited-state population of TIPS-pentacene in the triplet state increased with a high efficiency. Because the energy of the TIPS-pentacene triplet state is well matched with that of MAPbI₃ perovskite conduction band, the number of electrons transferred from TIPS-pentacene to MAPbI₃ perovskite increased as the triplet state population increased. We think that this increased number of electrons in MAPbI₃ perovskite conduction band can give rise to the enhancement of power conversion efficiency in MAPbI₃ perovskite solar cell.

In summary, we have demonstrated electron-transfer dynamics from the triplet state of TIPS-pentacene generated by singlet fission processes to MAPbI₃ perovskite conduction band. Direct observation of initial rise dynamics with a time constant of 1.1 ps in the TA decay profiles supports the fact that singlet fission processes occur in TIPS-pentacene/MAPbI₃ perovskite bilayer film. Moreover, the faster fluorescence lifetime and TIPS-pentacene cation band in the TA spectra indicate the existence of electron transfer in TIPS-pentacene/MAPbI₃ perovskite bilayer film. Finally, it was fully verified that the electron transfer is attributed to the triplet state of TIPS-pentacene generated by singlet fission processes through the analysis of TA decay profiles and the intensity ratio between 500 and 525 nm in TA spectra of TIPS-pentacene/MAPbI₃ perovskite bilayer film. This is the first study, to the best of our knowledge, showing the electron-transfer dynamics between TIPS-pentacene and MAPbI₃ perovskite, which can be applied to perovskite solar cells to improve solar cell efficiency. Therefore, we think that our results can provide useful information on the design of solar cells sensitized by singlet fission and the fabrication of new types of perovskite solar cells in the future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpclett.7b00072](https://doi.org/10.1021/acs.jpclett.7b00072).

Experimental details. Figure S1. Time-resolved fluorescence decay profiles of MAPbI₃ perovskite and TIPS-pentacene/MAPbI₃ perovskite bilayer films obtained using the TCSPC technique. Figure S2. TA spectra and decay profile of a MAPbI₃ perovskite film upon photoexcitation at 600 nm. Figure S3. TA spectra of the corrected TIPS-pentacene film, corrected MAPbI₃ perovskite film, and TIPS-pentacene/MAPbI₃ perovskite bilayer film. (PDF)

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Notes

The authors declare no competing financial interest.

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