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Solid-State Infrared Upconversion in Perylene Diimides Followed by Direct Electron Injection

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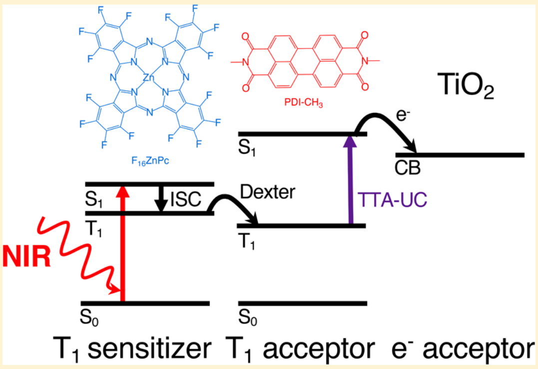
Supporting Information

ABSTRACT: In this contribution we demonstrate a solid-state approach to triplet−triplet annihilation upconversion for application in a solar cell device in which absorption of near-infrared light is followed by direct electron injection into an inorganic substrate. We use time-resolved microwave photoconductivity experiments to study the injection of electrons into the electron-accepting substrate (TiO_2) in a trilayer device consisting of a triplet sensitizer (fluorinated zinc phthalocyanine), triplet acceptor (methyl subsituted perylenediimide), and smooth polycrystalline TiO_2. Absorption of light at 700 nm leads to the almost quantitative generation of triplet excited states by intersystem crossing. This is followed by Dexter energy transfer to the triplet acceptor layer where triplet annihilation occurs and concludes by injection of an electron into TiO_2 from the upconverted singlet excited state.



One of the major factors limiting the energy conversion efficiency of single-junction solar cells to the Shockley−Queisser limit is the inability of the active materials to absorb photons with energies lower than their bandgap.[1] A promising approach to overcome this problem is the incorporation of an upconverter material that combines the energy of multiple low-energy photons into a single high-energy photon.[2] Theoretically, it has been predicted that this can increase the conversion efficiency of a single-junction solar cell to 50.7% for an ideal upconverter material.[3] The most commonly used upconverter materials are based on lanthanide compounds, for instance $NaYF_4:Er^{3+},Yb^{3+}$ and $NaYF_4:Er^{3+}$ with quantum efficiencies of 5% and 3% under monochromatic irradiation, respectively.[4] However, the upconversion efficiency of such materials is limited by their very narrow absorption spectrum and the fact that upconversion, being a higher-order process, requires high light intensities to be efficient.[5,6] An alternative approach is to exploit triplet−triplet annihilation upconversion (TTA-UC) using a combination of two different organic molecules as shown in Figure 1.[6−9] The process requires a chromophore, the triplet sensitizer (TS), that absorbs light in the near-infrared region and efficiently converts the initially formed singlet excited state into a triplet via intersystem crossing (ISC). These triplets are then transferred, by Dexter energy transfer, to a second molecule, the triplet acceptor (TA), with a lower-lying triplet state. If a sufficiently high concentration of excited-state triplet acceptors builds up, TTA-UC can occur, leading to the formation of a singlet excited state. Emission can then occur by the high-energy singlet. There are two distinct advantages to this approach over the use of rare earth materials. First, the absorption bands of organic chromophores are generally broad and can be tuned relatively easily by chemical modification. Second, the key intermediate is a triplet excited state that generally has a very long lifetime. The latter makes it possible

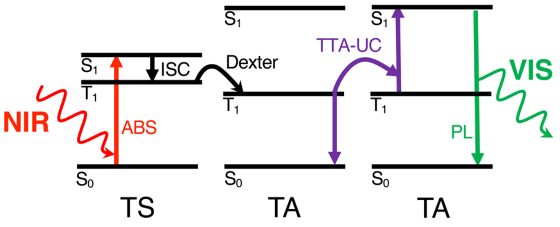


Figure 1. Scheme showing the TTA-UC process in a system composed of a triplet sensitizer (TS) and triplet acceptor (TA). Near-infrared light (NIR) is absorbed and creates a singlet excited state, S_1, that converts to a triplet state, T_1, via intersystem crossing (ISC). The triplet is transferred via Dexter energy transfer to the acceptor where it can undergo TTA-UC with a neighboring acceptor molecule in the T_1 state. Emission of visible light (VIS) can then occur via photoluminscence (PL).

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to build up a sufficient concentration of excited states, even under low light conditions.[9]

Upconversion by triplet−triplet annihilation has been extensively studied in solution, reaching quantum yields up to 32−38%.[10−12] While such efficiencies are impressive, it is rather undesirable from a technological point of view to use a solution-based system for large-scale applications. There have been attempts to show the same type of upconversion in rubbery polymer matrices, but the efficiency is limited by their poor molecular diffusion.[13,14] An additional complication of the upconversion by triplet−triplet annihilation is that it usually relies on re-emission from the upconverted singlet state. This introduces an additional loss mechanism in solar cells because the emitted photons have to again be absorbed efficiently by the active semiconducting material. In this work, we show that both these problems can be overcome by using a system that consists of two layers of crystalline materials where triplet energy transfer and triplet−triplet annihilation rely on exciton diffusion rather than molecular diffusion. After TTA-UC, the resulting singlet excited state directly injects an electron into a TiO_2 substrate, bypassing the emission and reabsorption steps. A recent review on solid-state upconversion discussed the different strategies involving supramolecular, macromolecular, and self-assembled systems to enable solid-state upconverrsion.[9] One strategy, explored by Hanson et al., involves the fabrication of a dye-sensitized system with triplet sensitizer anchored to the triplet acceptor which, in turn, is anchored to the electron acceptor TiO_2.[15−17] This upconverter architecture is similar to our approach, although there still is a dependence on the liquid medium containing electrolytes. One alternative solid-state upconversion system involves a spin-coated film consisting of triplet acceptor molecules that are doped with triplet sensitizer molecules to provide triplets and highly fluorescent energy collectors that collect upconverted singlets and recombine them radiatively. The doping of the triplet acceptor by both sensitizer and energy collector acts to mitigate singlet back energy transfer from the triplet acceptor to the triplet sensitizer because of a lack of physical contact between the triplet sensitizer and energy collector.[18] This promising study showed that exciton motion can provide reasonable upconversion in the solid state, although the system still relies on the emission of photons as a way to harvest the energy gained by upconversion. Similarly, another study on a solid-state upconversion system successfully demonstrated the prevention of singlet back-transfer from upconverted singlets in the triplet acceptor to the triplet sensitizer by using a neat layer of the triplet acceptor layer.[19]

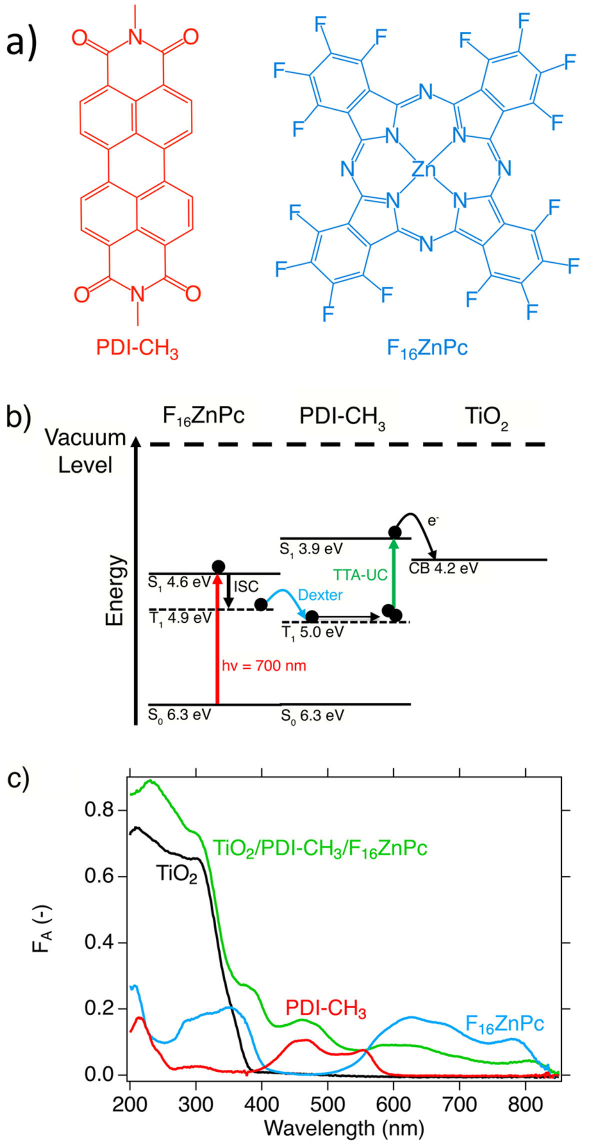

Figure 2. (a) Molecular structures of PDI-CH_3 and F_{16}ZnPc. (b) Schematic representation of the trilayer sample structure with triplet and singlet (HOMO and LUMO) energy levels for F_{16}ZnPc[21] and PDI-CH_3,[22−25] with respect to the conduction band edge (CB) of TiO_2.[26] (c) Attenuation spectra of the TiO_2/PDI-CH_3/F_{16}ZnPc (15/30 nm) trilayer (green) and single-layer films of TiO_2 (black), PDI-CH_3 (15 nm, red), and F_{16}ZnPc (30 nm, blue).

The solid-state upconversion system that we demonstrate here consists of two crystalline layers (Figure S1b) of fluorinated zinc phthalocyanine (F_{16}ZnPc) and perylenetetracarboxylic acid diimide (PDI-CH_3) whose structures are shown in Figure 2a. The layers are deposited on top of a smooth polycrystalline titanium dioxide (TiO_2) layer (Figure S1) that forms the trilayer system. F_{16}ZnPc acts as the near-infrared absorber and very efficient triplet sensitizer that has a triplet energy level that is appropriate to facilitate downhill energy transfer to PDI-CH_3 that acts as triplet acceptor where upconversion occurs. Finally, electrons are directly injected from the upconverted singlet excited state of PDI-CH_3 into TiO_2. The energy cascade leading to charge injection from upconverted singlets is schematically depicted in Figure 2b. Using this trilayer architecture, we show that near-infrared photon absorption at 700 nm photons can lead to charge injection into TiO_2 from PDI-CH_3, while it does not absorb near-infrared photons by itself. Instead, selective optical absorption in the near-infrared by F_{16}ZnPc, shown in Figure 2c, readily generates triplet states with high efficiency that transfer to PDI-CH_3 and undergo TTA-UC to singlet states that can thus provide charge injection. The system does not rely on molecular diffusion but uses exciton motion, which is proven to be sufficiently efficient in the crystalline materials used. This trilayer architecture involving intraband exciton transfer between triplet sensitizer and acceptor can be regarded as an example of the photoactive part of an intermediate band solar cell.[20]

N,*N*′-Dimethyl-3,4,9,10-perylenedicarboximide (PDI-CH_3) and zinc 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecafluoro-29H,31H-phthalocyanine (F_{16}ZnPc), powders were purchased from Sigma-Aldrich and used without further modification. The polycrystalline TiO_2-coated fused silica substrates (~90 nm thickness) were purchased from Everest Coatings Inc. and treated at 450 °C for 2 h in a furnace. A 15 nm layer of PDI-CH_3 and subsequently a 30 nm layer of $F_{16}ZnPc$ were thermally evaporated on top of TiO_2 films at 10^{-6} mbar as outlined in the Supporting Information. In this work we use time-resolved microwave photoconductance (TRMC) measurements to directly probe the mobile charges that are injected from the PDI-CH_3 film into the conduction band (CB) of TiO_2.[27] These TRMC measurements allow us to follow the electron injection process up to a millisecond time-scale.

In Figure 3a we show the time-resolved photoconductance of the TiO_2/PDI-CH_3/$F_{16}ZnPc$ trilayer system upon selective photoexcitation of the triplet sensitizer at 700 nm. The trilayer photoconductance exhibits a delayed rise over hundreds of microseconds that we corrected for intrabandgap excitation of the TiO_2 (see Figure S3 and the Supporting Information for details). In contrast, bilayer films of TiO_2/PDI-CH_3 and TiO_2/$F_{16}ZnPc$, also shown in Figure 3a, do not exhibit appreciable photoconductivity on the measured time scale, indicating that charge injection into TiO_2 does not occur upon photoexcitation at 700 nm. The absence of electron injection in the TiO_2/PDI-CH_3 bilayer is attributable to negligible optical absorption at 700 nm, although the electron affinity of PDI-CH_3, being 3.6 eV,[22−25] would allow charge injection into TiO_2 with an electron affinity of 4.2 eV.[26] In the case of the TiO_2/$F_{16}ZnPc$ bilayer, there is strong absorption by the $F_{16}ZnPc$ at 700 nm, but its electron affinity of 5.1 eV[21] is greater than that of TiO_2, preventing direct charge injection into the TiO_2 conduction band from either its lowest singlet or triplet state. Furthermore, we measured a trilayer system with reversed PDI-CH_3 and $F_{16}ZnPc$ ordering on the TiO_2 substrate. As evident in Figure 3a, this trilayer does not show any delayed rise, indicating the necessity of the specific ordering of the trilayer structure, i.e., triplet sensitizer−triplet acceptor−electron acceptor. We conclude that a sequential stepwise mechanism must be operative in which 700 nm light is absorbed by $F_{16}ZnPc$ forming an initial singlet excited state that is rapidly converted into a slightly lower-lying triplet state by intersystem crossing.[28,29] These triplet states are subsequently transferred to the PDI-CH_3 layer by Dexter energy transfer, leading to an accumulation of low-lying triplet excited states in this layer. The energy of these triplet states is lower than in $F_{16}ZnPc$; therefore, direct injection into TiO_2 is prohibited, as it is for $F_{16}ZnPc$.

However, in the PDI-CH_3 layer triplet−triplet annihilation can occur, mediated by triplet exciton diffusion, leading to the formation of a singlet excited state with high enough energy to inject an electron into the TiO_2 conduction band.[30−32] In a previous study we showed the injection of singlets in two PDI derivatives into TiO_2 that was used to estimate exciton diffusion lengths.[33] It should be noted that a dynamic equilibrium exists between the singlet and triplet populations in PDI-CH_3 that results from a balance in singlet fission and triplet−triplet annihilation upconversion. The dominant role of triplet exciton diffusion can be directly observed in the dynamics of charge injection in TiO_2.[34] This injection, and hence the growth of the photoconductivity, is seen to extend over hundreds of microseconds (see Figure 3a), much longer than the singlet lifetime.

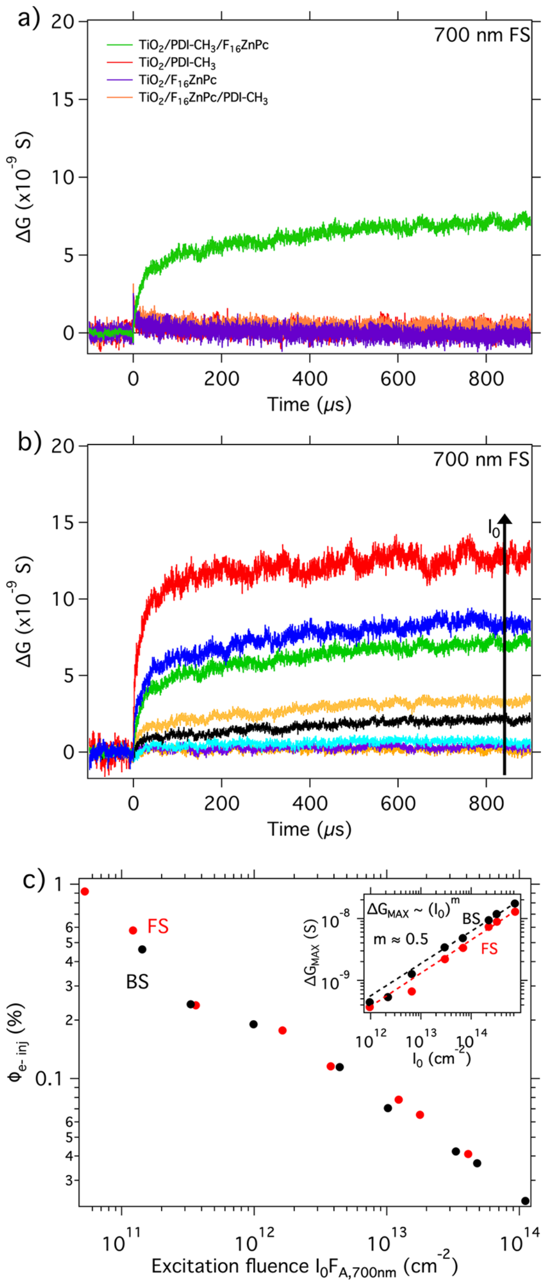

Figure 3. (a) Photoconductivity transients of two trilayer systems, TiO_2/PDI-CH_3/$F_{16}ZnPc$ (15/30 nm) and TiO_2/$F_{16}ZnPc$/PDI-CH_3 (30/15 nm), and bilayer films of PDI-CH_3 (15 nm), $F_{16}ZnPc$ (30 nm), and TiO_2 upon 700 nm excitation at an incident photon fluence of $I_0 = 2.3 \times 10^{14}$ photons/cm^2. (b) Fluence dependence of the TiO_2/PDI-CH_3/$F_{16}ZnPc$ (15/30 nm) trilayer photoconductivity transients at 700 nm for I_0 ranging from $I_0 = 9.5 \times 10^{11}$ to 7.4×10^{14} photons/cm^2. (c) Fluence-dependent yield of injection for the TiO_2/ PDI-CH_3/$F_{16}ZnPc$ trilayer. Inset: fluence dependence of the maximum signal ΔG_{MAX}.

In Figure 3b we show the photoconductance in the trilayer as a function of the incident photon fluence upon excitation of the $F_{16}ZnPc$ at 700 nm. An increase in the photon fluence increases the concentration of triplet states in the $F_{16}ZnPc$. This, in turn, leads to an increased PDI-CH_3 triplet concentration after Dexter energy transfer from the $F_{16}ZnPc$ that increases the formation of singlet states that can charge separate and inject an electron into the TiO_2 conduction band.

The maxima of the measured photoconductivity transients, ΔG_{MAX}, are plotted logarithmically as a function of the incident photon fluence, I_0, in the inset of Figure 3c. ΔG_{MAX} exhibits a square root dependence on the fluence over the entire fluence range. In contrast, solution-based triplet sensitizer and acceptor systems that involve monitoring the upconverter emission display a quadratic-to-linear transition of emission intensity with excitation fluence.[6] The quadratic-to-linear transition is due to diffusion-limited triplet−triplet encounters at low concentrations, while larger fluences saturate the triplet-state concentration such that the TTA-UC becomes optimal and the emission intensity scales linearly with the fluence. The square root dependence of injection efficiency on excitation fluence can be attributed to a combination of two factors. First, the fluence range that we use to probe the photoconducitivity is either not capable of saturating the PDI-CH_3 with triplet states, corresponding to the quadratic regime, or the lowest fluence used already ensures a saturated PDI-CH_3 triplet population, where all triplets find an annihilation partner and upconvert, corresponding to the linear regime. Second, the square root dependence indicates that a singlet decay process plays a role that may involve singlet fission which is known to occur effectively in PDI-CH_3.[35] We exclude second-order exciton recombination processes in F_{16}ZnPc as the cause of the square root fluence dependence as we do not observe a F_{16}ZnPc exciton density dependence on the maximum photoconductance. We tested this by photoexciting the trilayer from the front side (FS) and the back side (BS), corresponding to an excitation profile with a maximum at the F_{16}ZnPc/air and PDI-CH_3/F_{16}ZnPc interface, respectively. One would expect that excitation from the front, with creating a large concentration of F_{16}ZnPc excitons at the F_{16}ZnPc/air interface, allows for more exciton−exciton annihilation events to occur as excitons need to diffuse toward the PDI-CH_3/F_{16}ZnPc to transfer into the PDI-CH_3 in contrast to a reversed excitation profile in the back side excitation. However, we observe no such influence of excitation side on the ΔG_{MAX} fluence dependence, implying that second-order exciton recombination is not playing a role in the F_{16}ZnPc. Furthermore, diffusion limitations in the PDI-CH_3 and relatively low electron injection efficieny into the TiO_2 make it unlikely that second-order processes play a role in either PDI-CH_3 or TiO_2.[33] From ΔG_{MAX} we determined the yield of mobile electrons, $\phi_{\text{e-inj}}$, from absorbed photons as

$$\phi_{\text{e-inj}} = \frac{\Delta G_{\max}}{\Sigma\mu\beta e I_0 F_A} \tag{1}$$

where $\Sigma\mu = 2.3\ \text{cm}^2/(\text{V}\cdot\text{s})$ is the mobility of electrons in the conduction band of TiO_2 measured upon front side illumination (see Figure S2 and the Supporting Information for calculations), β a geometrical factor, I_0 the light intensity, and F_A the fraction of absorbed light at the wavelength of interest.[36] As shown in Figure 3c, the resulting $\phi_{\text{e-inj}}$ reaches maxima of 0.92% upon front side excitation and 0.46% for back side excitation at the lowest fluence measured. The almost linear fluence dependence of ΔG_{MAX} indicates that at the investigated excitation densities, all triplets find an annihilation partner and undergo TTA-UC, in analogy with the fluence dependence of the TTA-UC process in solution under high illumination conditions.[6] The observed trend for $\phi_{\text{e-inj}}$, i.e. decreasing upon increasing the fluence, can be explained by the occurrence of second-order recombination processes in the organic layers, e.g., singlet−singlet and/or triplet−triplet annihilation in PDI-CH, and/or second-order interfacial recombination. The low $\phi_{\text{e-inj}}$ is at least partially due to a low electron injection efficiency from PDI singlets that is commonly only a few percent.[33] We cannot determine the electron injection efficiency as photoexcitation of PDI-CH_3 leads to an unknown ratio of singlets and triplets and only singlets can charge separate. Therefore, we cannot quantify the amount of singlets that charge separate at the TiO_2 interface as a function of the absorbed amount of photons, i.e. the singlet charge separation yield for this specific sample. As a result, isolation of the TTA-UC efficiency from $\phi_{\text{e-inj}}$ by correcting for the singlet charge separation yield is also not possible. The presence of singlet fission in PDI-CH_3 also decreases the concentration of upconverted singlets and is another loss channel for the upconversion process. Finally, it is worth noting that TTA-UC requires two absorbed photons to generate one singlet excited state in PDI-CH_3, therefore defining the maximum number of injected electrons per absorbed photon to be 0.5. By setting this equal to 100% upconversion efficiency, we obtain an actual lower limit for the upconversion efficiency of 1.8%.

In order to directly confirm the formation of low-lying triplet excited states in PDI-CH_3 upon 700 nm excitation of F_{16}ZnPc, we have performed nanosecond transient absorption (TA) measurements. The changes in the optical absorption spectrum of PDI-CH_3 originating from ground-state bleach and triplet−triplet absorption are shown in Figure 4a. Upon 709 nm laser pulse excitation, a PDI-CH_3/F_{16}ZnPc bilayer on a sapphire substrate exhibits two characteristic transient absorption features: bleach of the ground-state absorption of PDI-CH_3 at 584 nm probe wavelength and a triplet−triplet absorption at 520 nm, as described previously.[37] This is corroborated by a decrease of the delayed rise in the photoconductance of the trilayer upon oxygen exposure that can be related to the well-known quenching of triplets by triplet oxygen (Figure S4).[37] In the transient absorption spectra of the respective monolayers we do not observe any change in the optical absorption spectrum under identical conditions. In solution, the triplet lifetime of zinc phthalocyanines is on the order of hundreds of microseconds, which makes the observation of a triplet absorption or ground-state bleach in the TA measurement likely.[38] However, the absence of a triplet absorption or ground-state bleach from F_{16}ZnPc indicates that energy transfer is complete and occurs within a few nanoseconds. The temporal evolution of the PDI-CH_3 bleach in a PDI-CH_3 layer only upon 480 nm and a PDI-CH_3/F_{16}ZnPc film upon 709 nm excitation is shown in Figure 4b in red and black, respectively. The signal is characterized by an instrument-limited rise, indicating that the PDI-CH_3 triplets are formed on a subnanosecond time scale and have a lifetime of $\tau_{T1} = 33$ ns.[35] The absence of an optical absorption caused by singlets or charge carriers at wavelengths above 620 nm indicates that triplets are the main photophysical species present in the PDI-CH_3 layer. This is corroborated by the identical decay of the bleach and triplet−triplet absorption (Figure S5). The discrepancy between the 33 ns triplet lifetime from ns-TA and the microsecond rise in the photoconductance observed in TRMC can be explained by the fact that only a relatively small portion of triplet excitons can upconvert and inject charges on the microsecond time scale. These can easily be detected in the TRMC experiment but are below the detection limit in the time-resolved optical absorption experiment.

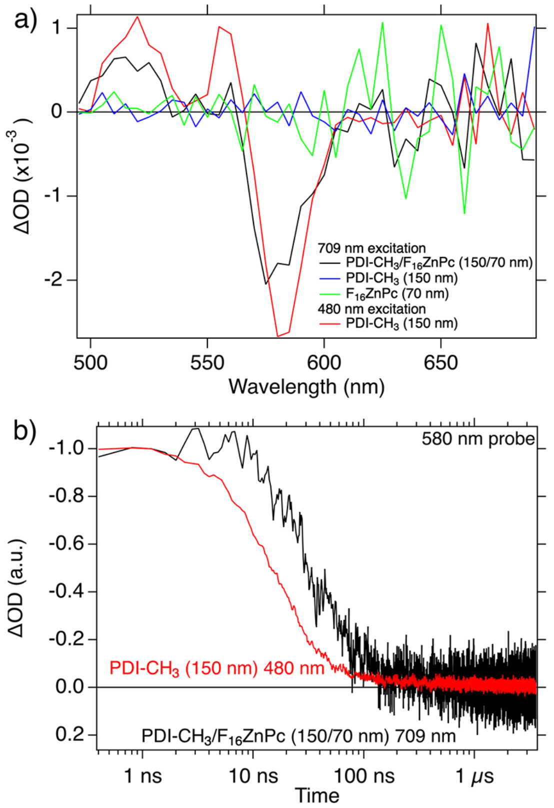

Figure 4. (a) Transient absorption spectra at t = 26 ns for a 150 nm thick PDI-CH$_3$ layer (blue), 70 nm thick F$_{16}$ZnPc (green), and 150/70 nm PDI-CH$_3$/F$_{16}$ZnPc bilayer (black) excited at 709 nm, and 150 nm thick PDI-CH$_3$ excited at 480 nm (red). (b) Temporal evolution of the PDI-CH$_3$ GSB in the PDI-CH$_3$ film upon 480 nm and PDI-CH$_3$/F$_{16}$ZnPc bilayer upon 709 nm excitation. The photon fluences upon excitation at 480 and 709 nm were 2.1 × 10^{15} and 1.5 × 10^{15} cm^{-2} at 709 nm, respectively.

In this work we have demonstrated the occurrence of the TTA-UC process in a TiO$_2$/PDI-CH$_3$/F$_{16}$ZnPc trilayer, where the singlet excited state formed by upconversion directly injects into the TiO$_2$. We show this by studying the photoconductance signal originating from selective 700 nm excitation of F$_{16}$ZnPc and subsequent electron injection from PDI-CH$_3$ into the TiO$_2$ conduction band. We observe a delayed electron injection occurring over a millisecond time scale. From the agreement between transient absorption spectra of a PDI-CH$_3$ film and a PDI-CH$_3$/F$_{16}$ZnPc bilayer upon excitation of the sensitizer, it is concluded that successful triplet energy transfer from the triplet sensitizer to the PDI acceptor occurs. The delayed rise of the TRMC signal is ascribed to PDI-CH$_3$ triplet states undergoing TTA-UC and resulting in upconverted PDI-CH$_3$ singlet states that charge separate at the TiO$_2$/PDI-CH$_3$ interface. In our system the absorbed photon to injected electron efficiency reaches a maximum of 1.8%, the lower limit of the upconversion efficiency. These results might be further improved by optimizing the thickness of the triplet sensitizer F$_{16}$ZnPc and triplet acceptor PDI-CH$_3$, in order to promote efficient exciton diffusion. Our experimental approach offers an effective tool to study the TTA-UC process in poorly luminescent materials, such as PDI-CH$_3$ thin films. The demonstrated trilayer structure may be tested in a photovoltaic device as the energy alignment would in principle allow hole and electron transport throughout the photoactive part.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.9b02361.

> Sample preparation and characterization; flash photolysis microwave conductivity; surface characterization; TiO$_2$ electron mobility determination; intraband gap-state correction in sensitized TiO$_2$ samples; air influence on delayed growth in photoconductance; ns-TA ground-state bleach and triplet absorption comparison; Figures S1−S5 (PDF)

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Notes

The authors declare no competing financial interest.

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