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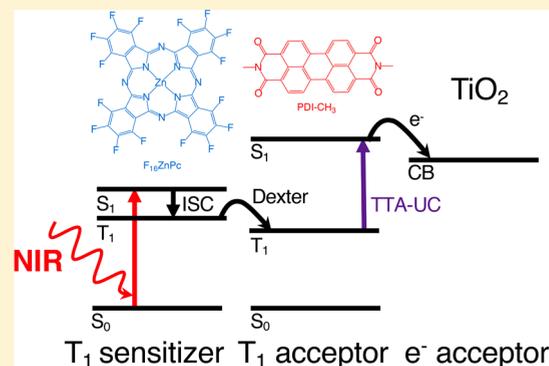
# Solid-State Infrared Upconversion in Perylene Diimides Followed by Direct Electron Injection

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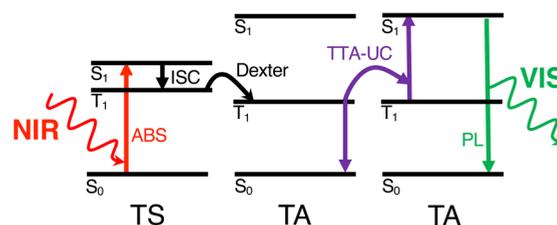
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## Supporting Information

**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 ( $\text{TiO}_2$ ) in a trilayer device consisting of a triplet sensitizer (fluorinated zinc phthalocyanine), triplet acceptor (methyl substituted perylenediimide), and smooth polycrystalline  $\text{TiO}_2$ . 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  $\text{TiO}_2$  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.<sup>1</sup> 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.<sup>2</sup> 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.<sup>3</sup> The most commonly used upconverter materials are based on lanthanide compounds, for instance  $\text{NaYF}_4:\text{Er}^{3+}, \text{Yb}^{3+}$  and  $\text{NaYF}_4:\text{Er}^{3+}$  with quantum efficiencies of 5% and 3% under monochromatic irradiation, respectively.<sup>4</sup> 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.<sup>5,6</sup> 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.<sup>6–9</sup> 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



**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 photoluminescence (PL).

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

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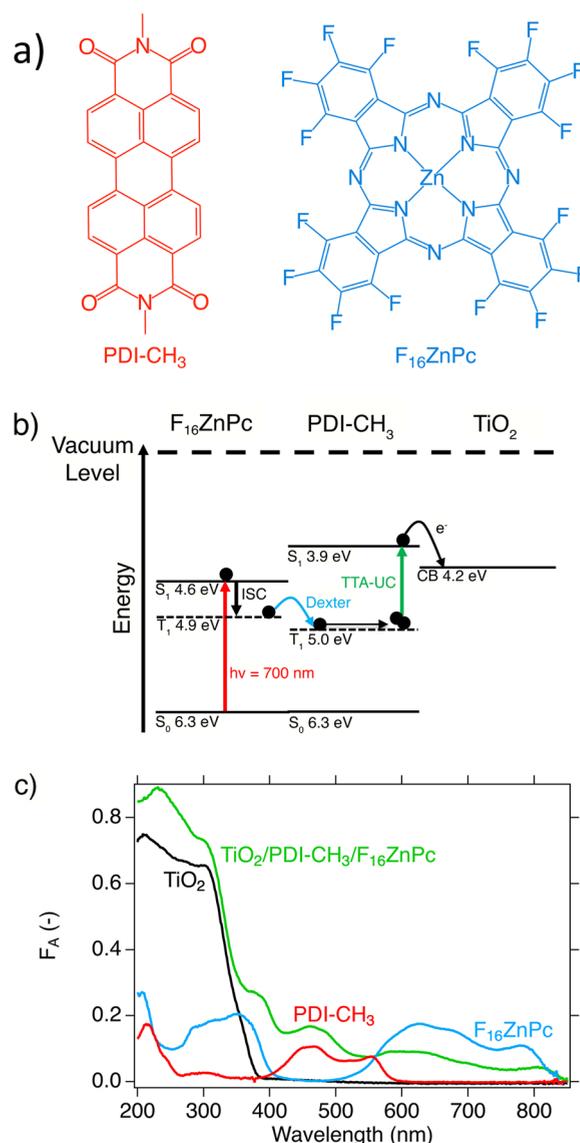
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to build up a sufficient concentration of excited states, even under low light conditions.<sup>9</sup>

Upconversion by triplet–triplet annihilation has been extensively studied in solution, reaching quantum yields up to 32–38%.<sup>10–12</sup> 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.<sup>13,14</sup> 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<sub>2</sub> 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 upconversion.<sup>9</sup> 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<sub>2</sub>.<sup>15–17</sup> 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.<sup>18</sup> 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.<sup>19</sup>

The solid-state upconversion system that we demonstrate here consists of two crystalline layers (Figure S1b) of fluorinated zinc phthalocyanine (F<sub>16</sub>ZnPc) and perylene-tetracarboxylic acid diimide (PDI-CH<sub>3</sub>) whose structures are shown in Figure 2a. The layers are deposited on top of a smooth polycrystalline titanium dioxide (TiO<sub>2</sub>) layer (Figure S1) that forms the trilayer system. F<sub>16</sub>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<sub>3</sub> that acts as triplet acceptor where upconversion occurs. Finally, electrons are directly injected from the upconverted singlet excited state of PDI-CH<sub>3</sub> into TiO<sub>2</sub>. 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



**Figure 2.** (a) Molecular structures of PDI-CH<sub>3</sub> and F<sub>16</sub>ZnPc. (b) Schematic representation of the trilayer sample structure with triplet and singlet (HOMO and LUMO) energy levels for F<sub>16</sub>ZnPc<sup>21</sup> and PDI-CH<sub>3</sub>,<sup>22–25</sup> with respect to the conduction band edge (CB) of TiO<sub>2</sub>.<sup>26</sup> (c) Attenuation spectra of the TiO<sub>2</sub>/PDI-CH<sub>3</sub>/F<sub>16</sub>ZnPc (15/30 nm) trilayer (green) and single-layer films of TiO<sub>2</sub> (black), PDI-CH<sub>3</sub> (15 nm, red), and F<sub>16</sub>ZnPc (30 nm, blue).

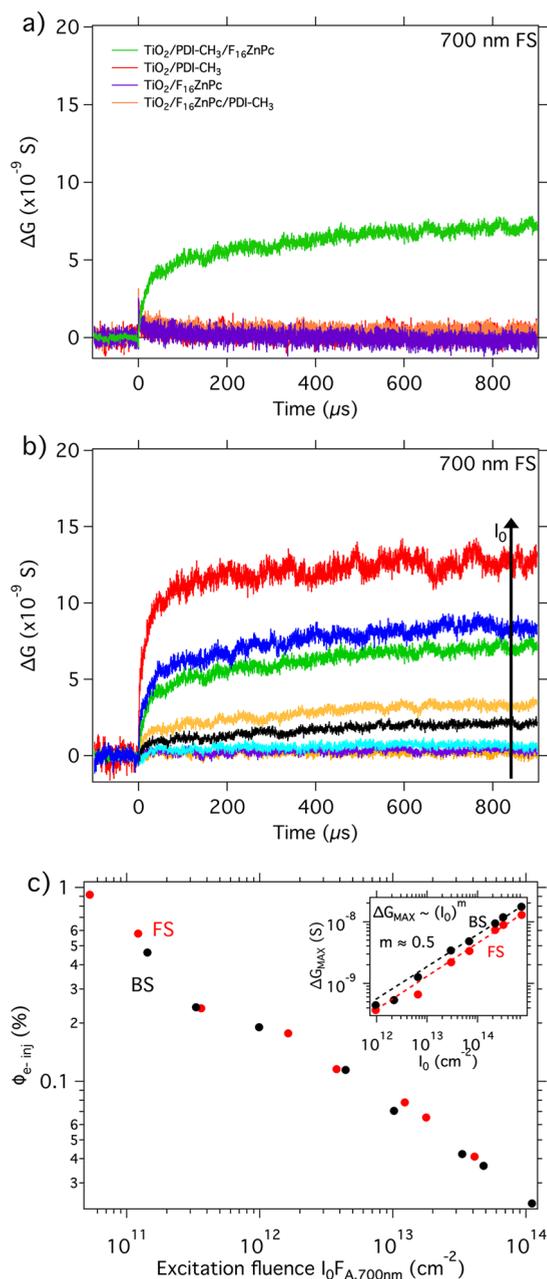
injection into TiO<sub>2</sub> from PDI-CH<sub>3</sub>, while it does not absorb near-infrared photons by itself. Instead, selective optical absorption in the near-infrared by F<sub>16</sub>ZnPc, shown in Figure 2c, readily generates triplet states with high efficiency that transfer to PDI-CH<sub>3</sub> and undergo TTA-UC to singlet states that can thus provide charge injection. The system does not rely on molecular diffusion but uses exciton transfer, 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.<sup>20</sup>

*N,N'*-Dimethyl-3,4,9,10-perylene-dicarboximide (PDI-CH<sub>3</sub>) and zinc 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecafluoro-29H,31H-phthalocyanine (F<sub>16</sub>ZnPc), powders were

purchased from Sigma-Aldrich and used without further modification. The polycrystalline TiO<sub>2</sub>-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<sub>3</sub> and subsequently a 30 nm layer of F<sub>16</sub>ZnPc were thermally evaporated on top of TiO<sub>2</sub> films at 10<sup>-6</sup> 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<sub>3</sub> film into the conduction band (CB) of TiO<sub>2</sub>.<sup>27</sup> 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<sub>2</sub>/PDI-CH<sub>3</sub>/F<sub>16</sub>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<sub>2</sub> (see Figure S3 and the Supporting Information for details). In contrast, bilayer films of TiO<sub>2</sub>/PDI-CH<sub>3</sub> and TiO<sub>2</sub>/F<sub>16</sub>ZnPc, also shown in Figure 3a, do not exhibit appreciable photoconductivity on the measured time scale, indicating that charge injection into TiO<sub>2</sub> does not occur upon photoexcitation at 700 nm. The absence of electron injection in the TiO<sub>2</sub>/PDI-CH<sub>3</sub> bilayer is attributable to negligible optical absorption at 700 nm, although the electron affinity of PDI-CH<sub>3</sub>, being 3.6 eV,<sup>22–25</sup> would allow charge injection into TiO<sub>2</sub> with an electron affinity of 4.2 eV.<sup>26</sup> In the case of the TiO<sub>2</sub>/F<sub>16</sub>ZnPc bilayer, there is strong absorption by the F<sub>16</sub>ZnPc at 700 nm, but its electron affinity of 5.1 eV<sup>21</sup> is greater than that of TiO<sub>2</sub>, preventing direct charge injection into the TiO<sub>2</sub> conduction band from either its lowest singlet or triplet state. Furthermore, we measured a trilayer system with reversed PDI-CH<sub>3</sub> and F<sub>16</sub>ZnPc ordering on the TiO<sub>2</sub> 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<sub>16</sub>ZnPc forming an initial singlet excited state that is rapidly converted into a slightly lower-lying triplet state by intersystem crossing.<sup>28,29</sup> These triplet states are subsequently transferred to the PDI-CH<sub>3</sub> 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<sub>16</sub>ZnPc; therefore, direct injection into TiO<sub>2</sub> is prohibited, as it is for F<sub>16</sub>ZnPc.

However, in the PDI-CH<sub>3</sub> 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<sub>2</sub> conduction band.<sup>30–32</sup> In a previous study we showed the injection of singlets in two PDI derivatives into TiO<sub>2</sub> that was used to estimate exciton diffusion lengths.<sup>33</sup> It should be noted that a dynamic equilibrium exists between the singlet and triplet populations in PDI-CH<sub>3</sub> 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<sub>2</sub>.<sup>34</sup> 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<sub>2</sub>/PDI-CH<sub>3</sub>/F<sub>16</sub>ZnPc (15/30 nm) and TiO<sub>2</sub>/F<sub>16</sub>ZnPc/PDI-CH<sub>3</sub> (30/15 nm), and bilayer films of PDI-CH<sub>3</sub> (15 nm), F<sub>16</sub>ZnPc (30 nm), and TiO<sub>2</sub> upon 700 nm excitation at an incident photon fluence of  $I_0 = 2.3 \times 10^{14}$  photons/cm<sup>2</sup>. (b) Fluence dependence of the TiO<sub>2</sub>/PDI-CH<sub>3</sub>/F<sub>16</sub>ZnPc (15/30 nm) trilayer photoconductivity transients at 700 nm for  $I_0$  ranging from  $I_0 = 9.5 \times 10^{11}$  to  $7.4 \times 10^{14}$  photons/cm<sup>2</sup>. (c) Fluence-dependent yield of injection for the TiO<sub>2</sub>/PDI-CH<sub>3</sub>/F<sub>16</sub>ZnPc trilayer. Inset: fluence dependence of the maximum signal  $\Delta G_{MAX}$ .

In Figure 3b we show the photoconductance in the trilayer as a function of the incident photon fluence upon excitation of the F<sub>16</sub>ZnPc at 700 nm. An increase in the photon fluence increases the concentration of triplet states in the F<sub>16</sub>ZnPc. This, in turn, leads to an increased PDI-CH<sub>3</sub> triplet concentration after Dexter energy transfer from the F<sub>16</sub>ZnPc that increases the formation of singlet states that can charge separate and inject an electron into the TiO<sub>2</sub> conduction band.

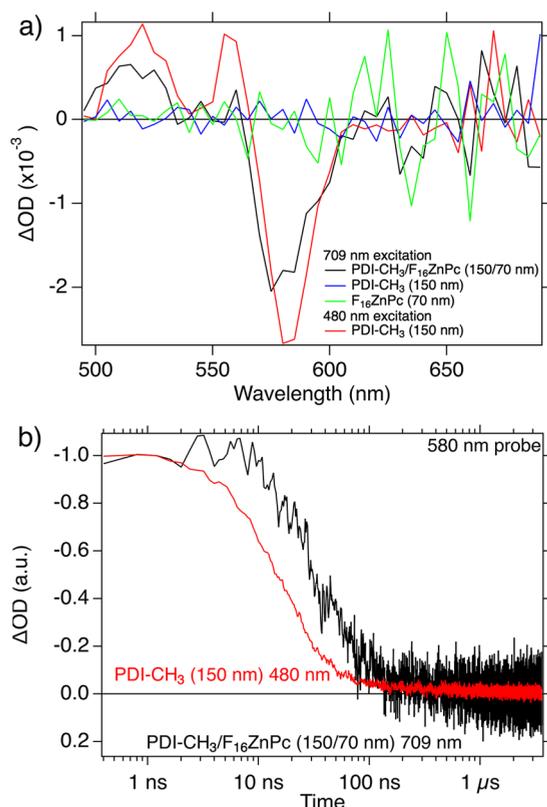
The maxima of the measured photoconductivity transients,  $\Delta G_{\text{MAX}}$ , are plotted logarithmically as a function of the incident photon fluence,  $I_0$ , in the inset of Figure 3c.  $\Delta G_{\text{MAX}}$  exhibits a square root dependence on the fluence over the entire fluence range. In 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.<sup>6</sup> 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 photoconductivity is either not capable of saturating the PDI-CH<sub>3</sub> with triplet states, corresponding to the quadratic regime, or the lowest fluence used already ensures a saturated PDI-CH<sub>3</sub> 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<sub>3</sub>.<sup>35</sup> We exclude second-order exciton recombination processes in F<sub>16</sub>ZnPc as the cause of the square root fluence dependence as we do not observe a F<sub>16</sub>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<sub>16</sub>ZnPc/air and PDI-CH<sub>3</sub>/F<sub>16</sub>ZnPc interface, respectively. One would expect that excitation from the front, with creating a large concentration of F<sub>16</sub>ZnPc excitons at the F<sub>16</sub>ZnPc/air interface, allows for more exciton–exciton annihilation events to occur as excitons need to diffuse toward the PDI-CH<sub>3</sub>/F<sub>16</sub>ZnPc to transfer into the PDI-CH<sub>3</sub> in contrast to a reversed excitation profile in the back side excitation. However, we observe no such influence of excitation side on the  $\Delta G_{\text{MAX}}$  fluence dependence, implying that second-order exciton recombination is not playing a role in the F<sub>16</sub>ZnPc. Furthermore, diffusion limitations in the PDI-CH<sub>3</sub> and relatively low electron injection efficiency into the TiO<sub>2</sub> make it unlikely that second-order processes play a role in either PDI-CH<sub>3</sub> or TiO<sub>2</sub>.<sup>33</sup> From  $\Delta G_{\text{MAX}}$  we determined the yield of mobile electrons,  $\phi_{\text{e-inj}}$ , from absorbed photons as

$$\phi_{\text{e-inj}} = \frac{\Delta G_{\text{max}}}{\Sigma\mu\beta eI_0F_A} \quad (1)$$

where  $\Sigma\mu = 2.3 \text{ cm}^2/(\text{V}\cdot\text{s})$  is the mobility of electrons in the conduction band of TiO<sub>2</sub> measured upon front side illumination (see Figure S2 and the Supporting Information for calculations),  $\beta$  a geometrical factor,  $I_0$  the light intensity, and  $F_A$  the fraction of absorbed light at the wavelength of interest.<sup>36</sup> 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  $\Delta G_{\text{MAX}}$  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.<sup>6</sup> 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.<sup>33</sup> We cannot determine the electron injection efficiency as photoexcitation of PDI-CH<sub>3</sub> 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<sub>2</sub> 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<sub>3</sub> 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<sub>3</sub>, 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<sub>3</sub> upon 700 nm excitation of F<sub>16</sub>ZnPc, we have performed nanosecond transient absorption (TA) measurements. The changes in the optical absorption spectrum of PDI-CH<sub>3</sub> originating from ground-state bleach and triplet–triplet absorption are shown in Figure 4a. Upon 709 nm laser pulse excitation, a PDI-CH<sub>3</sub>/F<sub>16</sub>ZnPc bilayer on a sapphire substrate exhibits two characteristic transient absorption features: bleach of the ground-state absorption of PDI-CH<sub>3</sub> at 584 nm probe wavelength and a triplet–triplet absorption at 520 nm, as described previously.<sup>37</sup> 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).<sup>37</sup> 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.<sup>38</sup> However, the absence of a triplet absorption or ground-state bleach from F<sub>16</sub>ZnPc indicates that energy transfer is complete and occurs within a few nanoseconds. The temporal evolution of the PDI-CH<sub>3</sub> bleach in a PDI-CH<sub>3</sub> layer only upon 480 nm and a PDI-CH<sub>3</sub>/F<sub>16</sub>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<sub>3</sub> triplets are formed on a subnanosecond time scale and have a lifetime of  $\tau_{\text{T1}} = 33 \text{ ns}$ .<sup>35</sup> 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<sub>3</sub> 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<sub>3</sub> layer (blue), 70 nm thick F<sub>16</sub>ZnPc (green), and 150/70 nm PDI-CH<sub>3</sub>/F<sub>16</sub>ZnPc bilayer (black) excited at 709 nm, and 150 nm thick PDI-CH<sub>3</sub> excited at 480 nm (red). (b) Temporal evolution of the PDI-CH<sub>3</sub> GSB in the PDI-CH<sub>3</sub> film upon 480 nm and PDI-CH<sub>3</sub>/F<sub>16</sub>ZnPc bilayer upon 709 nm excitation. The photon fluences upon excitation at 480 and 709 nm were  $2.1 \times 10^{15}$  and  $1.5 \times 10^{15}$  cm<sup>-2</sup> at 709 nm, respectively.

In this work we have demonstrated the occurrence of the TTA-UC process in a TiO<sub>2</sub>/PDI-CH<sub>3</sub>/F<sub>16</sub>ZnPc trilayer, where the singlet excited state formed by upconversion directly injects into the TiO<sub>2</sub>. We show this by studying the photoconductance signal originating from selective 700 nm excitation of F<sub>16</sub>ZnPc and subsequent electron injection from PDI-CH<sub>3</sub> into the TiO<sub>2</sub> 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<sub>3</sub> film and a PDI-CH<sub>3</sub>/F<sub>16</sub>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<sub>3</sub> triplet states undergoing TTA-UC and resulting in upconverted PDI-CH<sub>3</sub> singlet states that charge separate at the TiO<sub>2</sub>/PDI-CH<sub>3</sub> 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<sub>16</sub>ZnPc and triplet acceptor PDI-CH<sub>3</sub>, 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<sub>3</sub> 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/acsenerylett.9b02361>.

Sample preparation and characterization; flash photolysis microwave conductivity; surface characterization; TiO<sub>2</sub> electron mobility determination; intraband gap-state correction in sensitized TiO<sub>2</sub> 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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