Supporting Information

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

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Sample Preparation and characterization

Thin films of anatase TiO$_2$ of 90±10 nm thickness were purchased from Everest Coatings (Delft, The Netherlands). The films were prepared by chemical vapor deposition on top of 1 mm thick quartz plates. Subsequently, annealing at 450°C for two hours in air was performed to improve stoichiometry. The resulting crystallite size is 90±10 nm (see Figure S1). Thin films of PDI-CH$_3$ and F$_{16}$ZnPc powders were deposited on sapphire substrates by thermal evaporation in an AJA ATC Orion evaporator. Prior to deposition, the substrates and single layer TiO$_2$ film on a fused silica substrate (ESCO, 12 x 25 x 1 mm) were cleaned by an air plasma for 2 min at 1000 mtorr. During thermal evaporation, the powders were heated to their sublimation temperature (180-230°C) under high vacuum conditions (10$^{-7}$-10$^{-6}$ mbar) and was adjusted to an evaporation rate of 0.3 Å/s. The deposition rate was monitored using a quartz micro-crystal balance and a substrate holder rotated the substrates at 25
rpm to ensure film homogeneity. The resulting trilayer sample was annealed at 70°C for 1 hour. This preparation method ensures high reproducibility, homogeneity and controlled thickness of the PDI-CH₃ and F₁₆ZnPc films. In addition, following the PVD procedure described above, individual layers of F₁₆ZnPc and PDI-CH₃ and bilayers of TiO₂/ PDI-CH₃ and PDI-CH₃/F₁₆ZnPc were prepared for reference measurements.

The thin film surface morphology was probed with an NTEGRA Prima AFM atomic force microscopy (AFM) in tapping mode. X-ray diffractograms were acquired using a Brüker D8 X-ray diffractometer (Co Ka1 radiation, λ = 1.79 Å) and analysed with the Brüker program EVA. Steady state absorption spectra were obtained using a Perkin Elmer Lambda 1050 spectrometer with the sample placed inside of an integrating sphere to measure attenuation. Nanosecond time resolved transient absorption spectra were acquired using an LP920 transient absorption spectrophotometer of Edinburgh Instruments with pulsed probe light (7 ms) produced by a Xe lamp. The samples were excited by 4 ns (FWHM) laser pulses produced by an Ekspla NT 342B OPO pumped by a Q-switched Nd:YAG laser. To probe in the 495-690 nm region, we used a 495 nm long-pass filter when photoexciting the sample at 480 nm to neutralize scattered light, while upon 709 nm photoexcitation we used a 700 nm short pass filter.

**Flash Photolysis Microwave Conductivity**

The electron injection into TiO₂ was studied with the flash photolysis time resolved microwave conductivity (TRMC) technique. These TRMC measurements were performed on a home-built setup of which the operating principles are described elsewhere.¹ In this technique, optical excitation of the sample occurred via 3 ns full width half maximum (FWHM) laser pulses (λ = 240-2200 nm). The sample was probed by continuous X-band microwaves (~8.4 GHz) in a microwave resonant cavity cell that limited the instrumental response time to 18 ns. The sample chamber in the cavity cell was filled with N₂ to avoid oxygen expo-
sure. The fractional change in microwave power reflected \((\Delta P/P)\) is related to a change in photoconductance, \(\Delta G(t)\), as:

\[
\frac{\Delta P(t)}{P} = -K\Delta G(t)
\]  

(1)

In equation 1, \(K\) is the microwave frequency dependent sensitivity factor that has a predetermined value of \(40 \cdot 10^3 \, \text{S}^{-1}\) for the current experimental conditions. \(\Delta G(t)\) is directly proportional to the product of the charge carrier density \(n_i\) and mobility \(\mu_i\) according to:

\[
\Delta G(t) = e\beta L \sum_i n_i(t)\mu_i
\]  

(2)

In equation 2, \(e\) is the elementary charge, \(L\) the film thickness and \(\beta\) the ratio between the inner width and length dimensions of the microwave waveguide. The index \(i\) runs over all charged species present, \(i.e.\) electrons and holes both contribute to the photoconductance. The photoconductance transients can be deconvoluted for the instrumental response function using the cavity response function profile \((LP(t)):\)

\[
\Delta G_{\text{exp}}(t) = LP(t) \otimes \Delta G_0 \left( \sum_i c_i e^{-t/\tau_i} \right)
\]  

(3)

In equation 3, \(\Delta G_0\) is the initial photoconductance prior to charge carrier decay and \(\otimes\) indicates the convolution between \(LP(t)\) and \(\Delta G_0\). \(c_i\) and \(\tau_i\) are the exponent and decay time characteristic of the \(i\)-th transient decay component. The sum of all decay components account for all recombination processes occurring in the sample. \(\Delta G_0\) can be used to obtain a value for the product of the incident photon to charge carrier generation yield, \(\eta_0\), and the sum of electron and hole mobility, \(\sum \mu_i\), as \(3\):

\[
\frac{\Delta G_0}{\beta e I_0} = \eta \sum_i \mu_i
\]  

(4)

In equation 4, \(I_0\) is the measured incident photon fluence.
Surface characterization

Figure S1: a) AFM image of Pol-TiO$_2$. The crystallite size is approximately 100 nm. b) XRD diffractograms of Pol-TiO$_2$, a 100 nm PDI-CH$_3$ and a 200 nm F$_{16}$ZnPc film on fused silica and the fused silica substrate. The sharp peak at $2\theta = 29.8^\circ$ corresponds to a lattice spacing of 3.46 Å, typical for the anatase crystal unit.$^4$

TiO$_2$ electron mobility determination

We determined the electron mobility in TiO$_2$ using a previously used method.$^5$ In short, the maximum photoconductance signal at which no charge recombination has occurred, $\Delta G_0$, is equal to the product of the charge carrier generation yield, $\eta$, and the sum of the electron and hole mobility, $\sum \mu$, by the proportionality factor $\beta eI_0$: as described by equation 4. The hole
mobility in TiO$_2$ is assumed to be negligible compared to the TiO$_2$ electron mobility, $\mu_{e^-}$. We calculate the $\mu_{e^-}$ in TiO$_2$ by dividing the experimentally determined quantity $\Delta G_0/\beta e I_0$ by the fraction of absorbed photons at direct bandgap excitation in TiO$_2$ (300 nm), $F_{A,300\text{nm}}$, and by assuming that the absorbed photon-to charge carrier separation yield is unity, $\phi=1$:

$$\eta = \phi F_{A,300\text{nm}}$$

Therefore $\mu_{e^-}$ can be calculated as:

$$\mu_{e^-} = \frac{\Delta G_0}{F_{A,300\text{nm}} \beta e I_0}$$

Figure S2a and S2d show a plot of $\Delta G_0/\beta e I_0$ values, that are obtained from Figure S2a and S2b, as function of photon fluence. Upon front (FS) and back (BS) side direct bandgap excitation of TiO$_2$, $\Delta G_0/\beta e I_0$ amounts to 1.49096 and 1.4888 cm$^2$/Vs, respectively. Using the $F_{A,300\text{nm}}$ of 0.66 and 0.74 for FS and BS excitation gives $\mu_{e^-,FS} = 2.3$ cm$^2$/Vs and $\mu_{e^-,BS} = 2.0$ cm$^2$/Vs, respectively.
Figure S2: TRMC photoconductance $\Delta G$ transients as function of photon fluence upon 300 nm direct bandgap excitation of TiO$_2$ in front side (a) and back side (b) illumination. Plots of the maximum photoconductance $\Delta G_0/\beta e I_0$ as function of incident photon fluence. The dotted line, indicates the average maximum value that is used to determine the electron mobility in TiO$_2$, $\mu_e$, upon front side (c) and back side (d) illumination.
Sub-bandgap state correction in sensitized TiO$_2$ samples

We correct for intra-bandgap state absorption in TiO$_2$ at 700 nm photoexcitation by using a procedure used previously.\textsuperscript{5} This method involves subtracting the photoconductance transient, shown in Figure S3 of a single layer TiO$_2$ at 700 nm excitation from its respective TiO$_2$/PDI-CH$_3$/F$_{16}$ZnPc trilayer under identical excitation conditions. We scale the single layer TiO$_2$ trace with a weigh factor, F$_{SB}$, in order to match 100 ns kinetics. We note that the photoconductance transient of TiO$_2$ at 700 nm excitation was recorded only until 10 microseconds. In order to subtract it from the 1 ms transient, we extrapolated the latter part of the decay kinetics using a mono-exponential decay function.

![Figure S3](image)

**Figure S3:** Intrabandgap state correction of a trilayer photoconductance $\Delta G$ transients (red) obtained upon 700 nm back side (BS) illumination by an TiO$_2$ trace under identical illumination conditions (blue) that is scaled by a factor F$_{SB}$. The resulting trace is used to derive numbers for the electron injection efficiency (black).
Air influence on delayed growth in photoconductance

We studied the effect of air on the photoconductance by measuring the trilayer sample in an air atmosphere under identical conditions as in the case of an N₂ environment. In Figure S4 we observe only a very minute delayed photoconductance signal in air, which is in agreement with previous observations of oxygen quenching triplet states in perylene derivatives.⁶

![Figure S4: Photoconductance ΔG transient of a TiO₂/PDI-CH₃/F₁₆ZnPc (15/30 nm) tri-layer in N₂ (green) and in air (red) at 700 nm front side (FS) excitation (I₀ = 2.0·10¹⁴ photons/cm²).](image)

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⁶ Representative reference number.
ns-TA ground state bleach and triplet absorption comparison

Figure S5: Nanosecond TA transients of the trilayer at a probe wavelength of 520 (red) and 580 (black) nm, corresponding to the triplet absorption feature ($T_1-T_n$) and ground state bleach (GSB), respectively.

References

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