Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

BODIPY and Dipyrrin as Unexpected Robust Anchoring Groups on TiO_2 Nanoparticles

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Materials. All materials were purchased from Aldrich or Acros and used without further purification unless otherwise noted. Pyrrole was purchased from Aldrich, 98% purity, was distilled fresh before each synthesis. 2-methyl-1*H*- pyrrole, 95% purity, was purchased from Synthonix and also distilled fresh before each synthesis. Ti-Nanoxide T/SP paste was purchased from Solaronix. Anhydrous acetonitrile, >99.9% anhydrous and septum-sealed, was purchased from Honeywell.

Stability Measurements. For each of the stability traces a TiO_2 film on a glass substrate was first sensitized with **1**, **2**, or **4** according to the Procedure for Binding. First the time 0 UV-visible absorption measurement was taken of the sensitized film using the integrating sphere attachment. Then the film was placed in a vial with 4 mL of either water, dry acetonitrile, or a 1:1 mixture of the two. At each timepoint the film was removed, dried with a stream of air, and the absorbance was measured. As we were only interested in the effect of the solutions on stability, we did not include the time that the absorbance measurements took when reporting. Therefore, the time reported in the stability studies is indicative of time the films spent in each solvent.

Terahertz Measurements. A Spitfire Ace (Spectra Physics) that produces 800 nm pulses with a 35 fs FWHM at 1 kHz repetition rate was used. More detailed description of the instrument setup can be found in Regan et al.[1] The emitted beam is split into three separate beams; one is used for detection, one for probing the sample, and one which is used for optical excitation.[1] Excitation was done using 400 nm light, so the excitation beam was sent through a BBO to frequency double the pulse. For these experiments, samples were pumped at a power 100 mW. The terahertz probe is generated in an air plasma and data were collected using an Electro-Optic Sampling method with a Lock-in amplifier.[1] To perform an OPTP measurement, a THz pulse is measured without any photoexcitation. The change in peak THz (ΔTHz) is tracked relative to visible excitation (t_{pump}).

Surface Loading

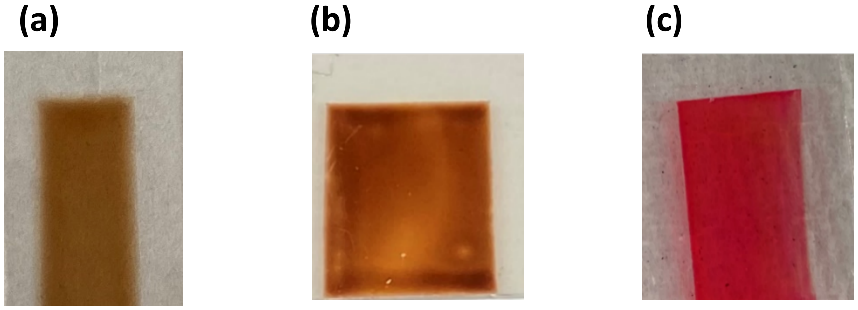

Figure S1. Photographs of (a) **1**; (b) **2** and (c) **4** on TiO_2 films.

Table S1. Loading numbers for the four molecules loaded onto TiO_2 films.

Molecule	Loading Number (mol cm^{-2} μm^{-1})
1	6.5×10^{-10}
2[a]	$(1.6 \pm 0.1) \times 10^{-9}$
3	6.7×10^{-11}
4	2.7×10^{-9}

a. Loading for **2** was averaged over three samples. Loading numbers were 1.59×10^{-9}, 1.61×10^{-9}, and 1.65×10^{-9}.

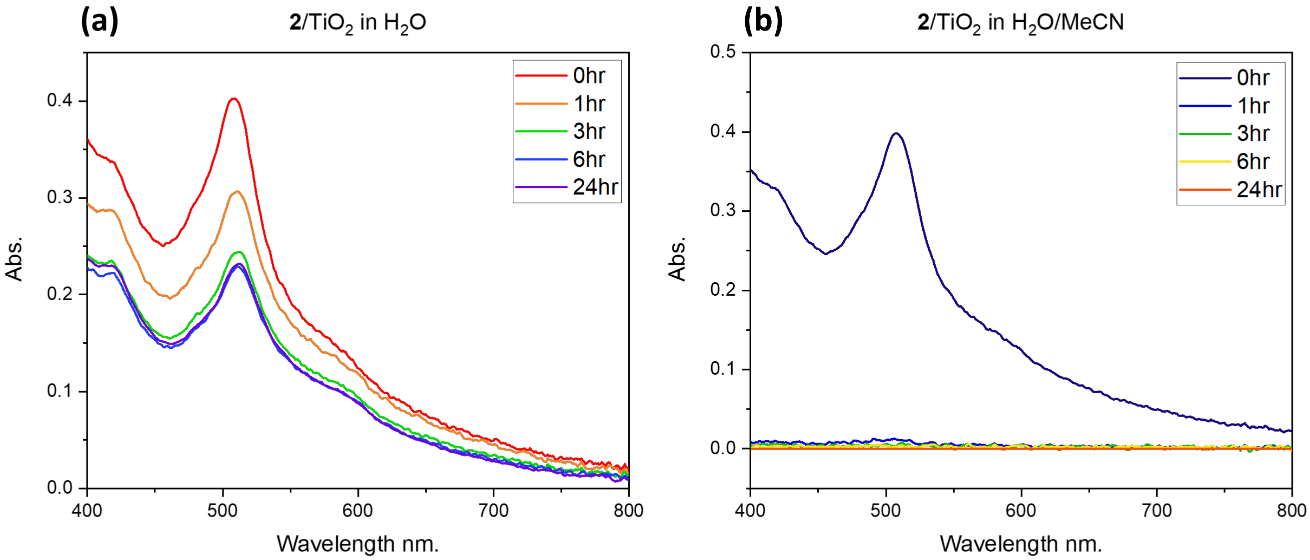

Figure S2. UV-visible spectra of **2**/TiO_2 in (a) H_2O and (b) H_2O/MeCN (1:1) over time. The decrease in the baseline is linear with the decrease in the peak which corresponds to the absorption of **2**.

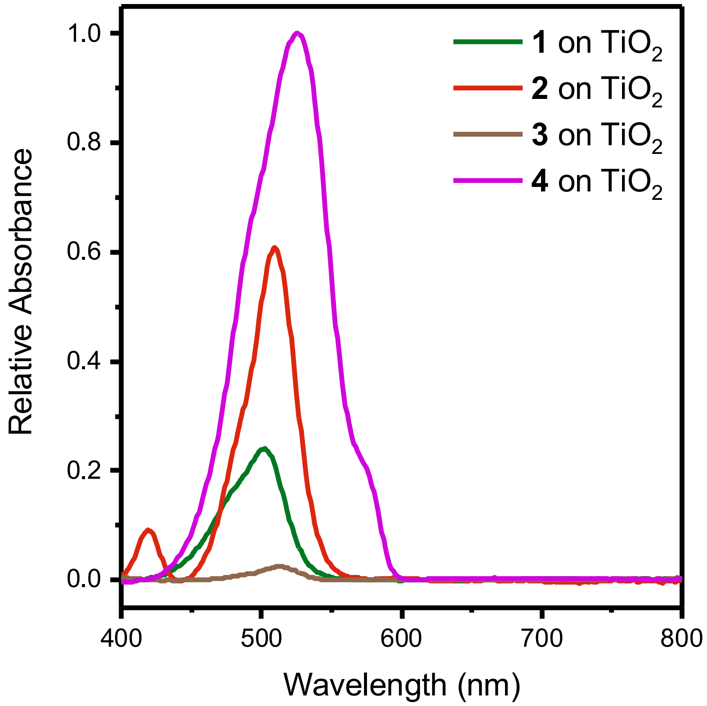

Figure S3. UV-visible spectra of molecules **1**–**4** on TiO_2. The baselines were removed to provide appropriate absorbances due to the dye molecules loaded on the surface.

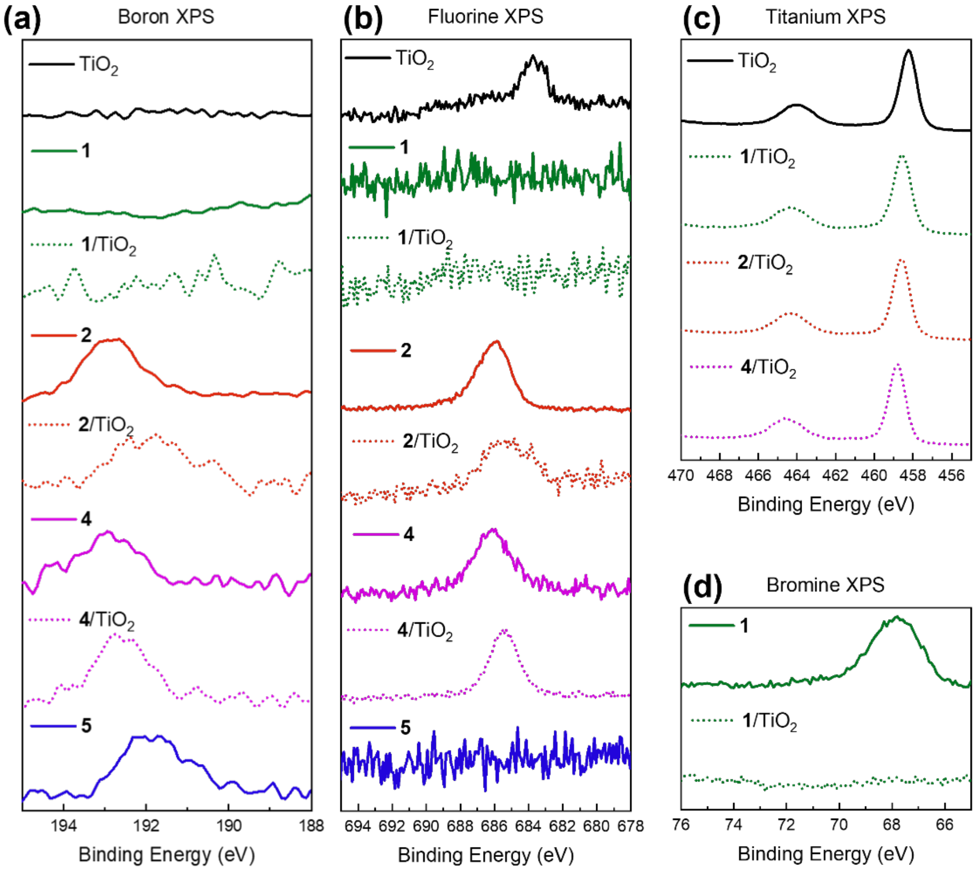

Figure S4. (a) XPS spectra of the boron binding energy for a bare TiO_2 film as well as **1**, **1**/TiO_2, **2**, **2**/TiO_2, **4** and **4**/TiO_2. The spectra were all collected in high power with 65 scans and smoothed using Savitzky-Golay smoothing.[2] (b) XPS spectra of the fluorine binding energy for the same samples as (a). The spectra were all collected in high power with 55 scans. (c) XPS spectra of the titanium binding energy in the four samples with TiO_2. The spectra were all collected in high power with 10 scans. (d) XPS spectra of the bromine binding energy of **1** and **1**/TiO_2 The spectra were collected in high power mode with 50 scans.

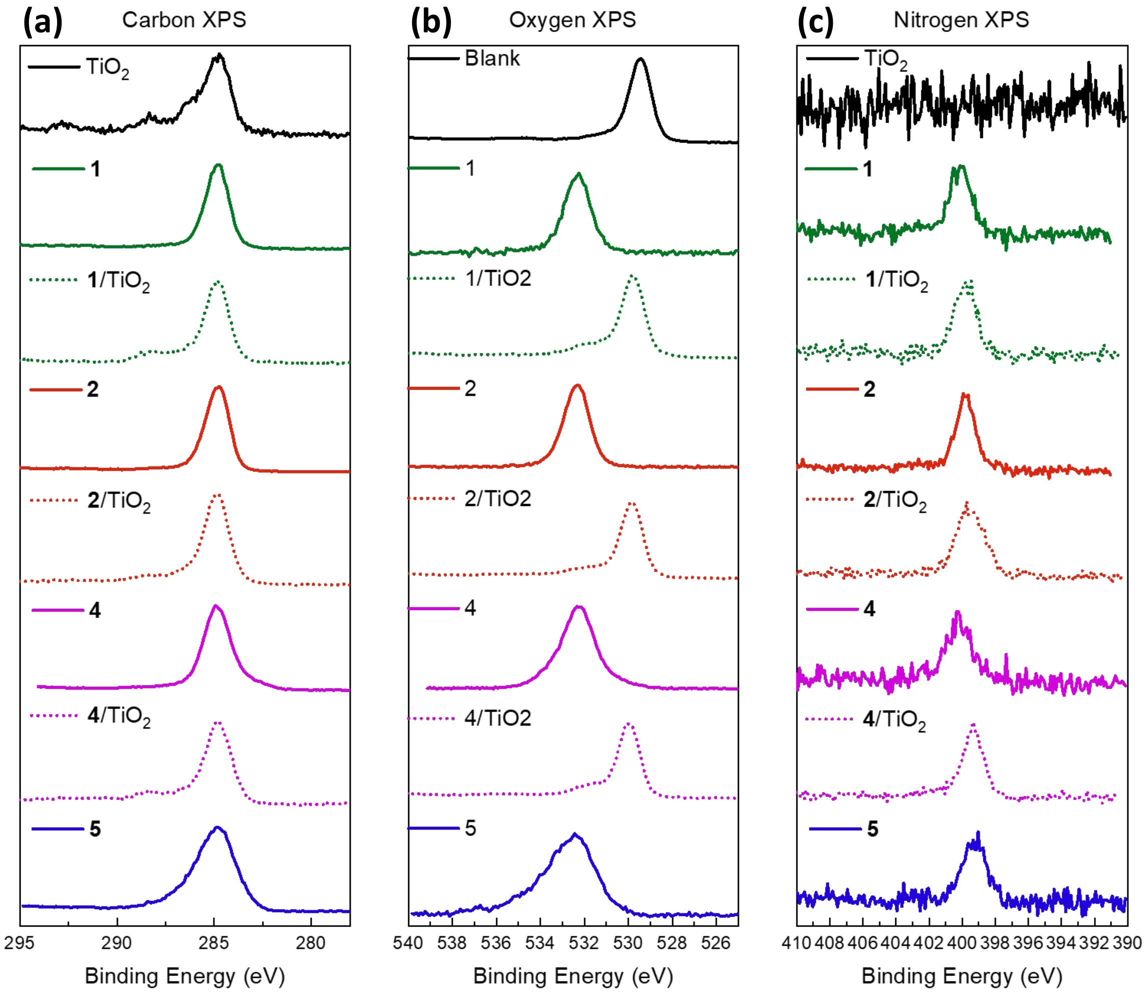

Figure S5. (a) XPS spectra of the carbon binding energy for a bare TiO_2 film as well as **1**, **1**/TiO_2, **2**, **2**/TiO_2, **4** and **4**/TiO_2. The spectra were all collected in high power with 10 scans. All spectra were charge-shift corrected to the adventitious carbon peak (284.8 eV); spectra in Figure S4 were subject to the same shift. (b) XPS spectra of the oxygen binding energy for the same samples as (a). The spectra were all collected in high power with 10 scans. (c) XPS spectra of the nitrogen binding energy in the same samples as (a) The spectra were all collected in high power with 10 scans.

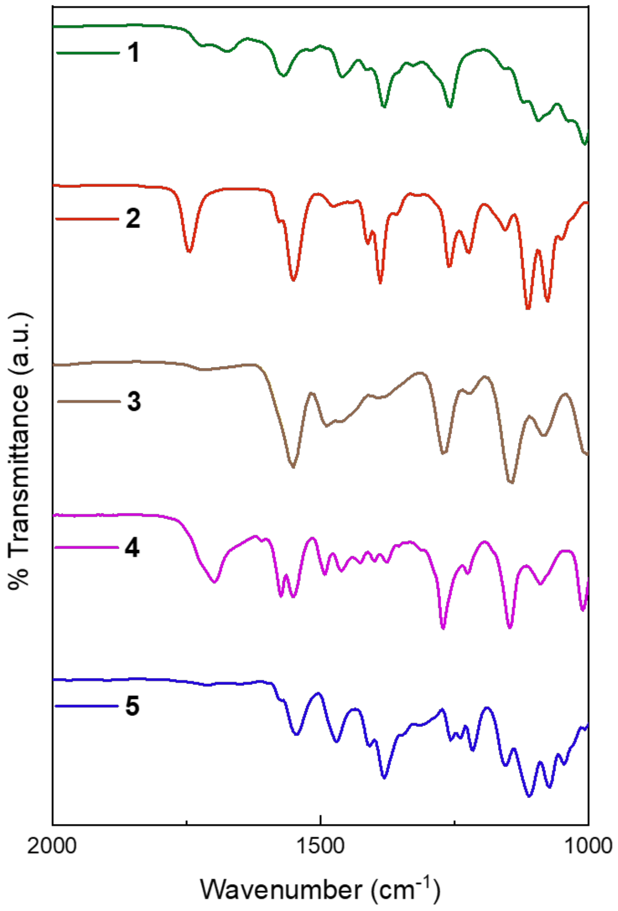

Figure S6. IR spectra of powder samples of all 5 molecules used in this study. Measured in transmission mode via ATR-FTIR.

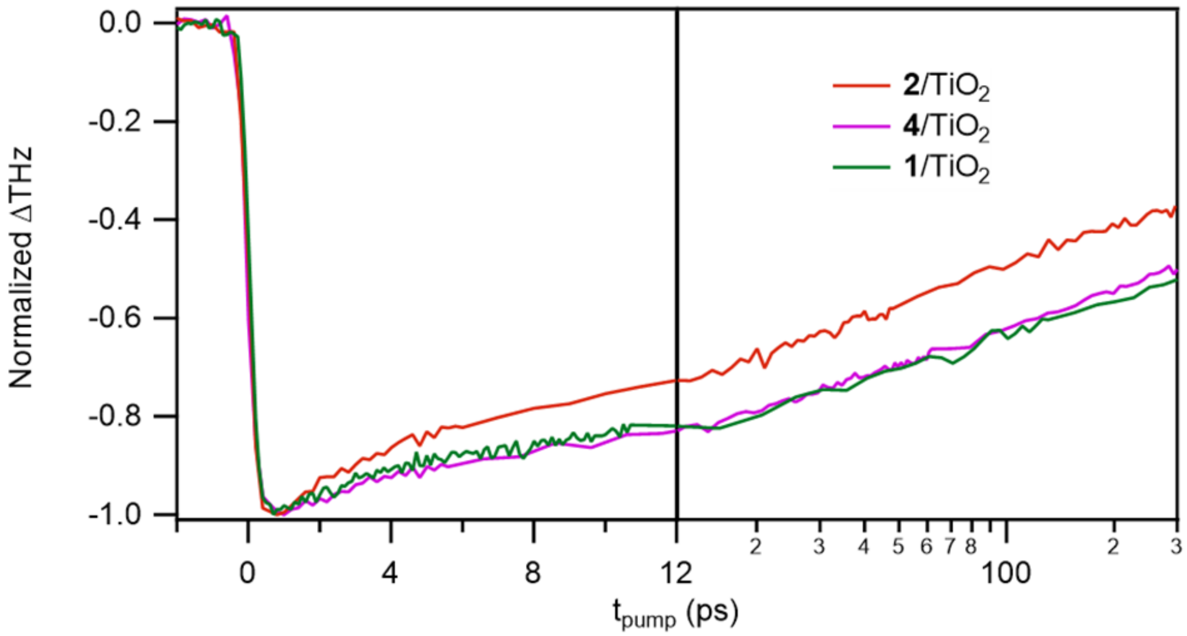

Figure S7. Normalized OPTP spectra for **1**, **2**, and **4** loaded onto TiO_2 to show the difference in recombination and/or trapping dynamics.

References:

1. K. P. Regan, C. Koenigsmann, S. W. Sheehan, S. J. Konezny and C. A. Schmuttenmaer, *J Phys Chem C*, 2016, 120, 14926-14933.
2. A. Savitzky and M. J. E. Golay, *Anal. Chem.*, 1964, 36, 1627-1639.