

Supplementary Information

Hole transfer dynamics from dye molecules to p-type NiO nanoparticles: effects of processing conditions

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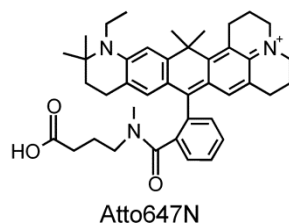


Fig. S1 Atto647N (C. Eggeling et al., *Nature* 2009, **457**, 1159)

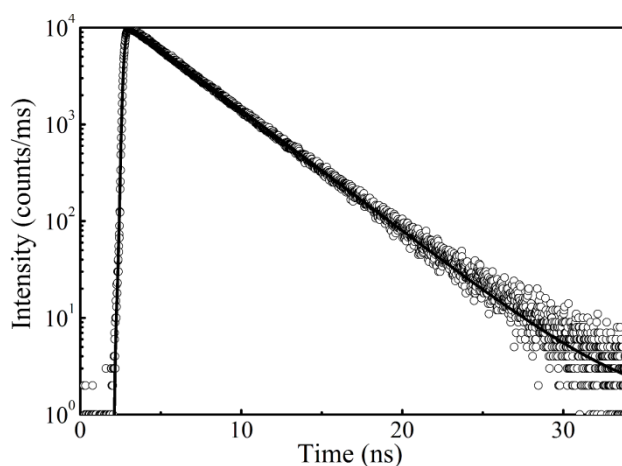


Fig. S2 Mono-exponential time-resolved fluorescence decay of Atto647N on ZrO₂ film with a lifetime component of 3.5 ns.

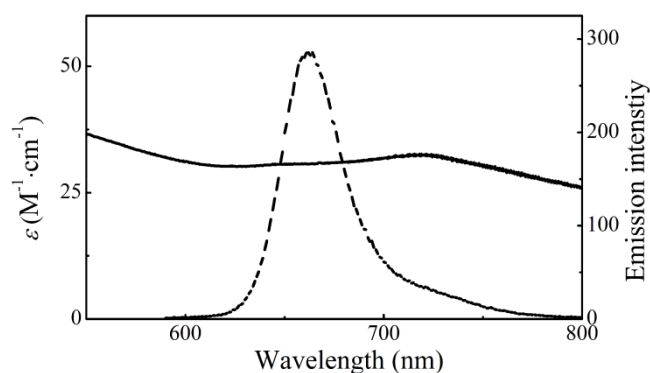


Fig. S3 Absorption spectrum (solid line) of NiO and fluorescence spectrum (dash line) of an aqueous solution of Atto647N.

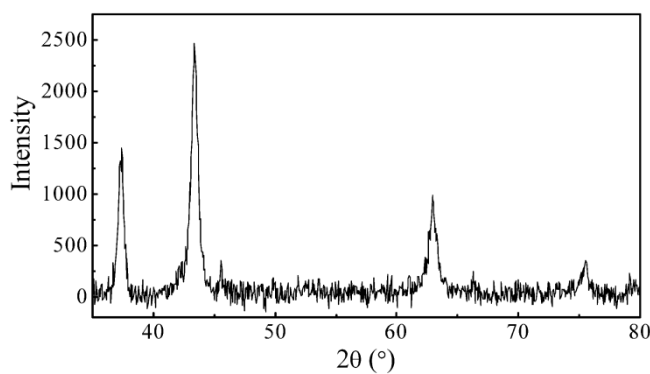


Fig. S4 XRD pattern of NiO NP.

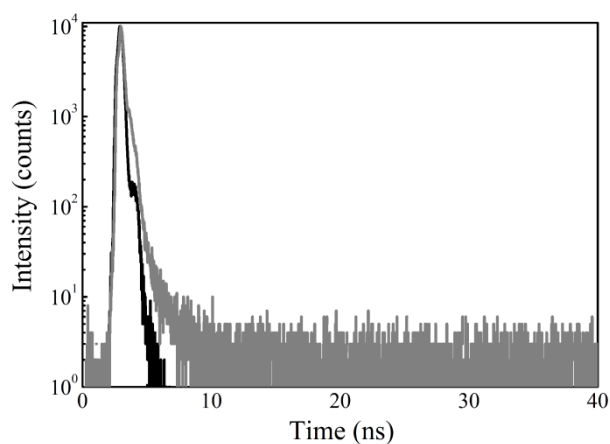


Fig. S5 Time-resolved fluorescence decay of a sample prepared by drop-casting a 10^{-4} M Atto647N on glass substrate (gray) and the instrument response function (black).

Femtosecond transient transmission spectroscopy

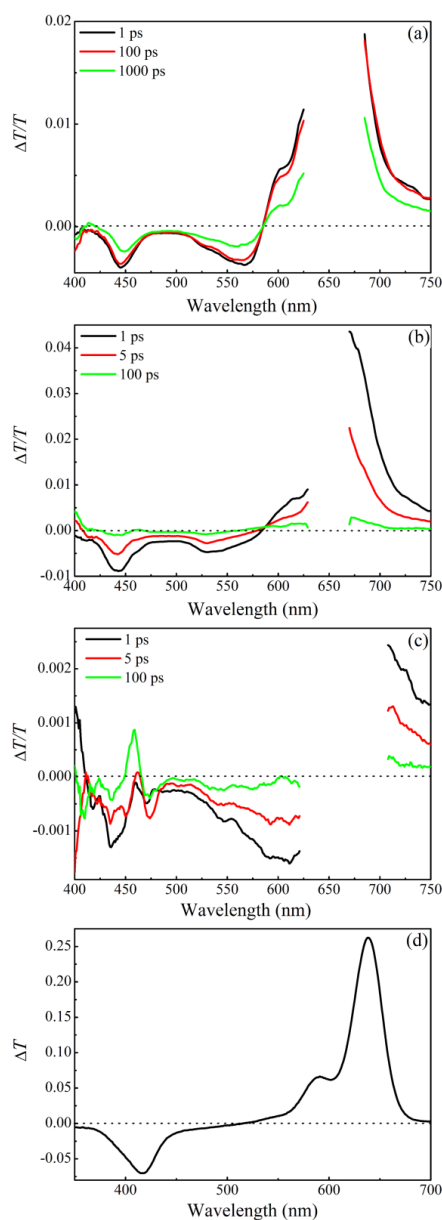


Fig. S6 (color) Transient transmission spectra of (a) an aqueous solution of Atto647N, (b) sample prepared by drop-casting $\sim 10^{-4}$ M Atto647N on a glass surface and (c) sample prepared by drop-casting $\sim 10^{-4}$ M Atto647N on a NiO NP film pre-annealed in air at different times after excitation at 650 nm. (d) Spectroelectrochemistry difference transmission spectrum of Atto647N in acetonitrile with potential set at -1.30 V vs. Pt wire.

The fs-transient transmission spectra, recorded following 650 nm laser pulse excitation, of an aqueous solution of monomeric Atto647N ($\sim 10^{-4}$ M) and solid-state samples of Atto647N prepared by drop-casting a $\sim 10^{-4}$ M dye solution on a glass surface and a NiO NP film are presented in Fig. S6. The TT spectrum of the dye solution (Fig. S6(a)) shows two excited-state bands in the range from 400-585 nm with maxima at 445 nm and 565 nm. The positive band found at wavelengths longer than 585 nm is due to the depletion of the ground state as it converts into an excited singlet state (*i.e.*, ground state bleaching). Within the time window of the measurements, it is observed that there is a slow decay in the intensity of the excited-state band probed at 450 nm (Fig. S6); corresponding to the relaxation of the excited-state to the ground-state of the dye molecule *via* fluorescence (*i.e.*, 3.8 ns from TCSPC measurement).

The TT spectrum of the solid-state sample prepared by drop-casting a $\sim 10^{-4}$ M solution on a glass cover-slip is shown in Fig. S6(b). The pump source populates exciton states of the aggregate with energies less than or close to the excitation wavelength (650 nm) which then quickly undergo relaxation to the lowest energy exciton state *via* rapid internal conversion. The positive $\Delta T/T$ band found at wavelengths > 585 nm is attributed to the ground state bleaching of both monomers and aggregates after pulse excitation. The negative TT bands centered at 443 nm and 530 nm are ascribed to a combination of the absorption of both the excited-state monomeric dye molecule and lowest energy exciton state of the aggregate. Clearly, for the solid-state sample (Fig. S6(b)), the decay of the band intensity of the excited-state with increasing delay times occurs much faster than that of the dye solution (Fig. S6(a)). The decay of transmittance change probed at a particular wavelength is fitted using a multi-exponential decay function with deconvolution:

$$\Delta T \propto \int_{-\infty}^t IRF(t') \sum_{i=1}^n A_i e^{-(t-t')/\tau_i} dt'$$

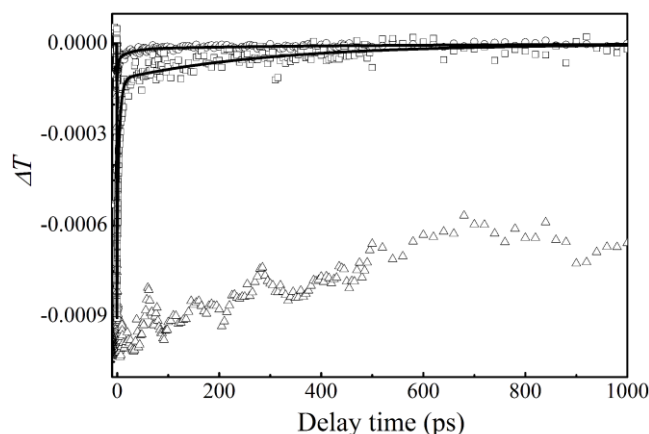


Fig. S7 Kinetic trace of (Δ) an aqueous solution of Atto647N probed at 450 nm, (\circ) a sample prepared by drop-casting a 10^{-4} M Atto647N solution on a glass surface probed at 450 nm and (\square) a sample prepared by drop-casting a 10^{-4} M Atto647N solution on a NiO NP film probed at 600 nm. Excitation wavelength = 650 nm. See Table S1 below for decay fitting parameters.

where A_i is the amplitude of the i th component, τ_i is the i th decay lifetime, and IRF is instrument response function that can be described as a Gaussian function with fwhm ~ 150 fs. The triple-exponential TT decay trace probed at 450 nm yielded lifetimes of 2 ps, 25 ps and 430 ps (Fig. S7). This suggests that the excited monomeric Atto647N undergoes an efficient relaxation process. Due to the close proximity between the dye molecules on the glass surface at high coverage, a plausible mechanism is the quenching of the excited state *via* dye-to-dye electron transfer.^{S1} From spectroelectrochemistry measurements, the radical anion Atto647N⁻ absorbs light in the wavelength region of 350-500 nm with maximum absorbance at 410 nm (Fig. 6(d)). The radical anion band is not observed in the TT spectrum (Fig. 6(b)); hence ruling out a dye-to-dye electron transfer mechanism. We propose that the ultrafast quenching of the excited-state of monomeric dye molecules, occurring in the picosecond time range, is due to efficient energy transfer to aggregates located close-by. A

heterogeneous distribution of the spatial separation and coupling between the two moieties leads to different energy trapping rates and results in the observed multi-exponential kinetic transient decay. Furthermore, the difference absorption (ΔOD) transients at 450 nm and 525 nm measured using a ns-flash photolysis spectrometer decayed too rapidly for the evolution of the excited-state to be studied within the temporal resolution of the instrument (Fig. S8).

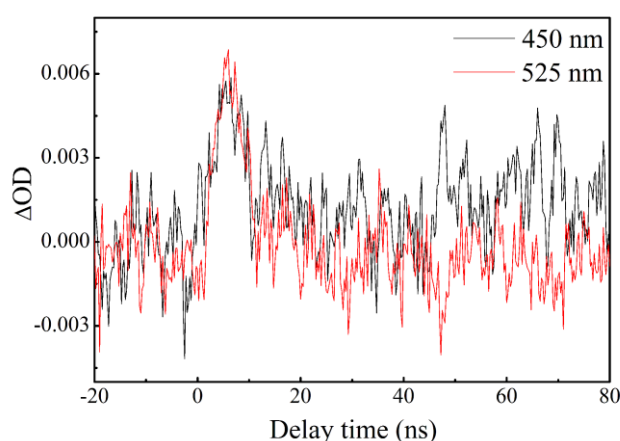


Fig. S8 (color) ns-flash photolysis kinetic trace of a sample prepared by drop-casting a 10^{-4} M Atto647N solution on a glass surface probed at 450 nm and 525 nm.

The difference transmission spectrum of the solid-state sample prepared by drop-casting a $\sim 10^{-4}$ M solution on a NiO NP film pre-annealed in air (Fig. 6(c)) exhibits a new negative band with maximum close to 610 nm. The TT signal is weak and noisy in the wavelength range 400-450 nm and no distinct band from Atto647N anion is seen in that region. This is because hole transfer from monomeric dye to NiO is significantly less efficient than quenching by energy transfer to aggregates, and Atto647N anions are not formed. The negative $\Delta T/T$ band observed in Fig. 6(c) is therefore ascribed to the absorption of anionic aggregate radicals formed as a result of rapid (< 1 ps) hole transfer from Atto647N aggregates to NiO. The charge recombination dynamics between the aggregate anion radical

and semiconductor is obtained by probing the TT intensity at 600 nm where contribution from the excited-state of monomer is minimal. In this case, the decay trace is triple-exponential with lifetimes of 0.6 ps, 4.7 ps and 298 ps (Fig. S7). The TT spectrum of oxidized NiO is not present due to its small extinction coefficient.^{S2}

Table S1: Fitting results of ultrafast transient absorption decay profiles of Atto647N molecules on glass and NiO film.

samples	decay time (amplitude)
Atto647N on glass ¹	2 ps (64%), 25 ps (21%), and 430 ps (15%)
Atto647N on NiO film ²	0.6 ps (34%), 4.7 ps (54%) and 298 ps (12%)

¹probed at 450 nm, ²probed at 600 nm.

References:

S1. P. Qin, J. Wiberg, E. A. Gibson, M. Linder, L. Li, T. Brinck, A. Hagfeldt, B. Albinsson and L. Sun, *J. Phys. Chem. C* 2010, **114**, 4738.

S2. (a) A. Morandeira, J. Fortage, T. Edvinsson, L. Le Pleux, E. Blart, G. Boschloo, A. Hagfeldt, L. Hammarström and F. Döbel, *J. Phys. Chem. C* 2008, **112**, 1721; (b) L. Le Pleux, A. L. Smeigh, E. Gibson, Y. Pellegrin, E. Blart, G. Boschloo, A. Hagfeldt, L. Hammarström and F. Odobel, *Energy Environ. Sci.* 2011, **4**, 2075.

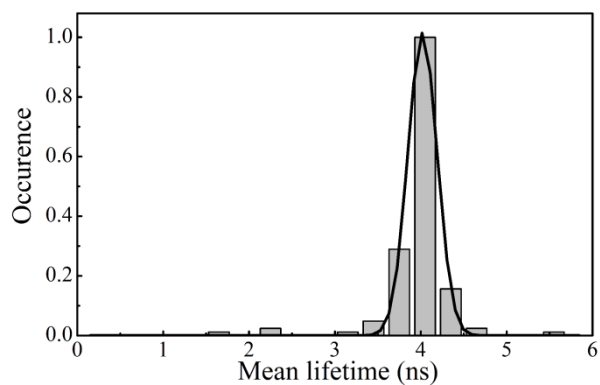


Fig. S9 Histogram of the mean fluorescence lifetimes of 131 single Atto647N molecules on glass.

Movie 1 caption: Defocused wide-field fluorescence microscopy movie of single Atto647N molecules spin-coated on a NiO NP film.