Supporting Information

Atomic Scale Perspective of Ultrafast Charge Transfer at a Dye-Semiconductor Interface

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S1. Sample Preparation

ZnO nanoparticles were synthesized using a method reported by Bauer *et al.*¹ Briefly, 50 mmol tetramethylammonium hydroxide (25% solution in methanol from Sigma-Aldrich) was added to a suspension of 50 mmol zinc acetate dihydrate (Merck) in 100 ml anhydrous ethanol (Sigma-Aldrich). The resulting sol was refluxed at 80 °C for 30 minutes and left overnight in the fume hood to let the particles precipitate. Next, the extra solvent was decanted and particles were washed with ethanol to remove excess tetramethylammonium hydroxide. The ZnO colloid was then concentrated using a rotary evaporator until it was visibly viscous. Thin films were obtained by spin coating 0.20 ml of this suspension on a Si(100) substrate followed by drying at 60 °C and sintering in air at 380 °C for 30 minutes. The average particle size was approximately 16 nm, the average film thickness around ~500 nm. After ozone/UV cleaning, the thin films were immersed in 0.2 mM solution of N3 Ru dye (Aldrich) in absolute ethanol for 24 hours. The resulting dye sensitized films were then thoroughly rinsed with ethanol, dried in an air stream and stored in the dark. Before being transferred into the experimental chamber, the samples were mildly baked at 60 °C for ~2 days reaching a background pressure of $\sim 8 \times 10^{-10}$ mbar.

S2. Time-resolved XPS experiment

The experiment was performed at the Soft X-ray Materials Science (SXR) instrument² of the Linac Coherent Light Source (LCLS).³ An ultrashort (FWHM $\leq$ 50 fs) laser pulse with a center wavelength of 535 nm electronically excited the Ruthenium dye complex. The transient electronic structure was probed by a time-delayed X-ray pulse (FWHM $\leq$ 100 fs)⁴ centered at 850 eV using a monochromator.⁵ The angle between the laser and X-ray beams was kept small ($\leq$ 3 mrad) in order to avoid a timing walk-off between the two pulses. Femtosecond time-resolved inner shell photoelectron spectra of the sample in the region of the Ru 3d_{3/2,5/2} lines were recorded with a hemispherical electron analyzer (Scienta R3000). The relative electron kinetic energies of all N3/ZnO XPS peaks were determined by varying the acceleration voltage of the electron analyzer. Absolute binding energies were defined by pinning the Ru 3d_{5/2} line to the value given by Schnadt and co-workers (280.6 eV)⁶. A detailed description of the instrument is given elsewhere.⁷ The uncertainty in the pump-probe time-delay Δt was ~280 fs (FWHM) due to

the inherent timing jitter between the optical laser and the LCLS.⁸ The background pressure during the experiment was $\sim 10^{-8}$ mbar.

Space charge effects were minimized by attenuating the LCLS beam with a combination of Mg foils and an adjustable gas attenuator. The X-ray pulse intensity at the sample was on the order of $\sim 10^6$ photons/pulse. The pump laser pulse energies were 170 μ J - 200 μ J. The estimated pump laser and X-ray spot sizes on the film of dye-sensitized nanocrystals were $\sim 0.28 \times 5$ mm² and $\sim 0.25 \times 5$ mm², respectively. The asymmetric shape of the spots results from a shallow incidence angle ($\sim 87^\circ$) geometry, which is chosen to optimize the count rate while minimizing the impact of sample damage and space charge effects. The pump pulse repetition rate was 60 Hz while X-ray pulses were generated at 120 Hz, enabling an alternating pump-on/pump-off - X-ray probe scheme that strongly suppresses the impact of any long-term variations in the experimental conditions on the difference between pump-on and pump-off spectra. On average, less than one photoelectron was detected for each X-ray pulse.

S3. Sample damage measurements and control

Sample damage is a central concern for measurements on non-replenishing, light-sensitive targets such as films of dye-sensitized nanocrystals. Extensive sample damage measurements using both visible femtosecond laser pulses and X-ray pulses were performed prior to the LCLS experiment in order to determine the sample exposure limits.

Laser damage induced by the visible pump-pulse was determined by laboratory-based femtosecond fluorescence microscopy experiments. Femtosecond laser pulses with a 532 nm center wavelength were focused to a spot size of ~ 3 μ m diameter on the sample and the laser-induced fluorescence intensity was monitored in real time for a variety of laser pulse energies. The time-dependent decay of the fluorescence signal reflects the degree of photobleaching and damage of the dye as a function of integrated photon flux. X-ray damage was analyzed in a series of X-ray photoelectron spectroscopy (XPS) measurements at the ambient pressure XPS beamline 11.0.2 of the Advanced Light Source (ALS).

The dominating sample damage mechanism in the LCLS experiment was deterioration of the dye molecules by exposure to the visible femtosecond pump pulses. Target damage by the

strongly attenuated, low repetition rate LCLS X-ray pulses was negligible on the timescale of the experiment. Despite the short LCLS X-ray pulse duration no nonlinear X-ray processes were induced due to the significant attenuation of the X-ray beam necessary to avoid space charge effects.

In order to minimize the impact of target damage by the pump laser, each sample spot was exposed for only 10-15 minutes before moving to a new spot. At a 60 Hz laser repetition rate, this procedure limited the total number of laser pulses to $\leq 54,000$ and the total number of photons to $\leq 3 \times 10^{19}$ per sample spot. The integrated energy of this photon flux is equivalent to less than five hours exposure to natural sunlight. Potential residual target damage effects in the pump-on/pump-off difference spectra were effectively eliminated by operating the pump laser at half the repetition rate of the LCLS probe pulses (60 Hz and 120 Hz, respectively) and recording pump-on and pump-off spectra simultaneously.

S4. Data analysis

S4.1. Determination of transient chemical shifts

The time-dependent changes in the XPS spectra in the range of the C 1s/Ru 3d photolines (Fig. 2 in main article) are analyzed based on the assumption that the pump laser-induced spectral variations are predominantly caused by a shift of the $\text{Ru}3d_{3/2,5/2}$ doublet associated with the metal center of the N3 dye. The resulting fit function has therefore only two free fit parameters: the transient chemical shift ΔE_b of the Ru $3d_{3/2,5/2}$ lines and the fraction F of molecules that exhibit this shift in binding energy. A prerequisite for this fit routine is an accurate description of the Ru 3d signals. Since the Ru $3d_{3/2}$ line is entirely masked by the dominant pyridine C 1s peak (Fig. 2A in main article), it has to be modeled based on the measured position of the Ru $3d_{5/2}$ line, the spin-orbit-splitting between the doublet components, their lifetime broadening (0.17 eV for Ru $3d_{5/2}$ and 0.59 eV for the Ru $3d_{3/2}$ line⁹), and the Ru $3d_{3/2}$: Ru $3d_{5/2}$ intensity ratio. The energy splitting and the intensity ratio are extracted from reference data collected at a synchrotron using clean ruthenium metal samples for which the Ru 3d doublet is fully resolved (Fig. S1).

Figures S1a,b show Ru 3d photoemission spectra from a Ru(0001) single crystal obtained with (a) un-polarized $\text{MgK}\alpha$ radiation at 1254 eV photon energy, and (b) p-polarized

synchrotron radiation at 635 eV photon energy. The spectrum in (c) is from an amorphous Ru sample, recorded with p-polarized 380 eV synchrotron radiation. The binding energies were calibrated by measuring the position of the Fermi level. The measured line shapes of the Ru 3d doublet are approximated by Voigt profiles (green (cross-hatched) and blue shaded) consisting of a convolution of the natural Lorentzian line shapes with Gaussian profiles that model both the inhomogeneous broadening of the photoemission lines as well as the instrumental response of the electron spectrometer. The fit results important for our model are listed in Table S1.

Despite the significantly different photon energies, polarizations and sample conditions the extracted spin-orbit energy splittings and intensity ratios are almost identical. This suggests that the mean values (4.17 eV peak splitting; 1.51 peak ratio) are also representative for the N3 Ru 3d doublet in the LCLS experiment at 850 eV photon energy.

The XPS apparatus function of the LCLS experiment is obtained by fitting a convolution of a Lorentzian with a fixed FWHM of 0.17 eV (lifetime broadening),⁹ and an asymmetric Gaussian function on top of a Shirley background¹⁰ to the well-resolved Ru 3d_{5/2} line of the LCLS laser-off spectrum (Fig. S2). The resultant response function exhibits a 1.31 eV FWHM “low-binding-energy-tail” and a 1.53 eV FWHM “high-binding-energy-tail”. Using this LCLS XPS apparatus function, the difference spectrum (pump-on - pump-off) can be modeled with a function $D(\Delta E_b, F)$ to obtain the transient chemical shift ΔE_b and the excitation yield F .

The results for the two available LCLS datasets are shown in Figs. 2 and S3. The photoemission data are normalized to the total area of the spectra. Both datasets reveal a transient binding energy shift of the Ru 3d_{3/2,5/2} doublet on the order of ~2 eV.

S4.2. Robustness of the fit routine and correction of the transient surface photovoltage effect

The robustness of the data analysis and, in particular, of the fit procedure to determine the transient chemical shift of the Ru 3d doublet and the laser-induced transient surface photovoltage effect has been carefully tested based on two quantitative criteria, the reduced χ_r^2 merit function,¹¹ and the Abbe criterion.¹²

The pump laser induces a transient surface photovoltage (SPV)¹³ in the sample that manifests itself in a rigid shift of the entire laser-on XPS spectrum by ΔSPV to lower binding energies compared to the laser-off reference spectrum. The magnitude of ΔSPV has to be derived from the data. Figure S4 shows a simulation that illustrates the impact of the SPV on the measured difference spectrum. A relative small displacement is sufficient to cause a distinct difference spectrum. Therefore, the measured laser-on spectrum has to be corrected by shifting it by ΔSPV in the opposite direction of the SPV effect in order to isolate the transient chemical shift of the inner-shell photoemission lines. Qualitatively, the charge-transfer induced chemical shift of the Ru 3d doublet (Fig. S4b, dashed curve) and the transient SPV effect (Fig. S4b, red solid and green dash-dotted curves) can be distinguished by the different positions of the corresponding extrema in the laser-on/laser-off difference curves and the relative intensities of the peaks in the difference spectra. The chemical shift of the Ru 3d doublet induces maximum differences at the centers of the Ru 3d peaks while the SPV induced shift of the entire spectrum induces maximum differences where the peaks have maximum gradients. The peaks in the laser-on/laser-off difference spectra induced by the SPV effect scale with the heights of all peaks contained in the laser-off spectrum, leading to much larger difference peaks in the range of the dominant pyridine C 1s line compared to the Ru 3d_{5/2} line (Fig. S4b, red solid and green dash-dotted curves). In contrast, the differences induced by the chemical shift of the Ru inner shell lines scale according to the relative intensities of the Ru 3d doublet only, leading to *smaller* difference peaks in the range of the most intense pyridine C 1s line compared to the Ru 3d_{5/2} line (Fig. S4b, dashed curve) as observed in the experiment after correcting for the SPV effect (Figs. 2, S3). Note that, in particular, the data set recorded at 1000 fs pump-probe delay, albeit affected by more statistical scatter than the 500 fs data set, also exhibits a more pronounced difference signal in the range of the Ru 3d_{5/2} peak than in the range of the Ru 3d_{3/2} and C1s peaks, supporting the interpretation of the difference signal at shorter delays. In order to further exclude SPV-induced artifacts, we ensured that kinetic energy shifts of the entire spectrum do not induce any peak shape variations within the precision of the experiment. This was done by varying the nominal kinetic energy setting of the electron analyzer by 5 eV, i.e. by more than an order of magnitude more than the SPV-induced shifts. The comparison of the original with the shifted electron spectra does not indicate any kinetic energy dependent peak shape variations.

To determine ΔSPV , a series of identical fits have been performed with the laser-on spectrum shifted step-wise relative to the laser-off spectrum between consecutive fits. This fit series results in a sequence of chemical shifts ΔE_b as a function of the SPV correction ΔSPV as shown in Fig. S5 for the $\Delta t=500$ fs dataset. The reliability of the obtained ΔE_b values is tested by two methods: the χ_r^2 merit function (“reduced χ^2 ”)¹¹ and the Abbe criterion.¹² The χ_r^2 merit function is defined as

$$\chi_r^2 = \frac{\sum_{i=1}^N \left(\frac{R(i)}{\sigma_i} \right)^2}{N-M} = \frac{\chi^2}{N-M} \quad (\text{S1})$$

Here, N is the number of data points used in the fit, $R(i)$ is the difference between the fit result and the i^{th} data point, σ_i is the uncertainty of the i^{th} data point, and M is the number of free fit parameters.

The Abbe criterion¹² is defined as

$$\text{Abbe} = \frac{1}{2} \times \frac{\sum_{i=1}^{N-1} [R(i+1) - R(i)]^2}{\sum_{i=1}^N [R(i)]^2} \quad (\text{S2})$$

based on the residuals $R(i)$ described above. Both the χ_r^2 merit function and the Abbe criterion are quantitative measures that provide a stringent test for the absolute fit reliability beyond the common minimal χ^2 criterion. The criteria effectively test whether the deviations between the data and the fit function are dominated by systematic or statistical errors, the former indicating a problem, the latter the desired result.

A statistically meaningful fit result and, in particular, an appropriate number of free fit parameters are marked not only by a minimum of χ_r^2 , but this minimum value has to be close to 1.¹¹ The value of the Abbe criterion (Equation S2) may indicate three limiting cases:¹² systematically correlated ($\text{Abbe} = 0$) or anti-correlated ($\text{Abbe} = 2$) residuals usually indicate an inadequate model function. Statistically distributed residuals are marked by $\text{Abbe} = 1$, which, therefore, identifies a fit result compatible with the ideal assumption that the difference between the model curve and the data points is described by random noise.

Both the χ_r^2 merit function (Fig. S5a) and the Abbe criterion (Fig. S5b) respond sensitively to the ΔSPV shift, enabling an accurate determination of the SPV correction. At $\Delta\text{SPV} = -348$ meV, a clear minimum of the χ_r^2 merit function at $\chi_r^2=1.02$ coincides with the Abbe

peak-value of $Abbe = 1.03$, indicating a high degree of confidence in the validity of the fit results at this SPV correction. In principle, the SPV correction ΔSPV can be included as a free fit parameter. However, in the interest of clarity and transparency of the data analysis procedure, the SPV correction is discussed independently here. The same tests have been applied to the $\Delta t = 1000$ fs dataset. We note that a variety of other methods to determine the SPV correction and the transient chemical shift of the Ru 3d doublet has been tested extensively, leading to the same results as noted above within the given uncertainties.

Fig. S1. Ru 3d photoelectron spectra (circles) acquired using a Ru(0001) crystal with (a) unpolarized MgK α radiation (1254 eV) and (b) p-polarized 635 eV synchrotron radiation. (c) Synchrotron spectrum obtained from an amorphous Ru sample at a photon energy of 380 eV (p-polarization). The green (cross-hatched) and blue shaded areas indicate Voigt profiles used to model the peaks. The red solid curves are the overall fit results.

Fig. S2. Determination of the LCLS XPS apparatus function by fitting a convolution (red solid line) of a 0.17 eV FWHM Lorentzian line shape with an asymmetric Gaussian profile to the well-resolved Ru 3d_{5/2} photoline. The blue dashed curve indicates a Shirley background included in the fit.

Fig. S3. Fit results for $\Delta t=1000$ fs, 200 μ J pump pulse energy. (a) Smoothed photoelectron spectra recorded with the pump laser on (red, solid) and off (blue, dashed), normalized to the total intensity between 274 eV and 294 eV binding energy. (b) Difference between pump-on and pump-off spectra (gray circles) and fit curve $\mathbf{D}(\Delta E_b, F)$ (green solid).

Sample	h ν ; polarization	Spin-orbit splitting (eV)	Ru3d _{5/2} :Ru3d _{3/2} intensity ratio
Clean Ru(0001)	1254 eV; unpol.	4.17	1.51
Clean Ru(0001)	635 eV; p-pol.	4.18	1.54
Sputtered Ru(0001)	380 eV; p-pol.	4.15	1.49

Table S1. Spin-orbit splitting and peak ratios retrieved from the fit shown in Fig. S1.

Fig. S4. Simulated impact of improper SPV corrections on the difference spectra. (a) Simulated laser-off C1s/Ru3d spectrum of N3 (blue dashed line) shifted along the binding energy axis by -13 meV and +13 meV (red solid and green dash-dotted line, respectively). The resulting difference spectra with respect to the unshifted spectrum are depicted as red solid and green dash-dotted lines in (b). For comparison, the black dashed line represents a simulated difference spectrum for a transient Ru 3d shift ($F = 5\%$ and $\Delta E_b = 2\text{ eV}$) only.

Fig. S5. Testing the robustness of the fit procedure and SPV correction ($\Delta t=500$ fs). (a) Retrieved values for the transient Ru 3d shift ΔE_b as a function of the applied SPV correction ΔSPV (black circles). The χ_r^2 merit function of the fits is shown as red dots. (b) Dependence of the Abbe criterion (blue dots) of the transient ΔE_b fit results on the applied SPV correction ΔSPV .

S5. Theoretical modeling by constrained density functional theory (CDFT)

In order to help interpret the measured transient core-level shifts at the Ru 3d_{5/2} edge, a number of theoretical calculations based on first principles density functional theory¹⁴⁻¹⁵ (DFT) were carried out. The theoretical model consists of an N3 dye molecule chemisorbed on a non-polar ZnO (10 $\bar{1}$ 0) surface. The goal of the theoretical calculations is to identify a length scale of charge-separation between the electron and the hole in the photo-excited (pumped) system that is consistent with the measured Ru 3d_{5/2} core-level shift (ΔE_b).

S5.1. N3-ZnO interface: Bonding geometry

Firstly, various bonding motifs of the dye molecule on the non-polar ZnO (10 $\bar{1}$ 0) surface were investigated in order to determine the most thermodynamically favourable binding geometry. For this purpose, the non-polar surface is modeled as an infinite two-dimensional slab that is six atomic layers thick within a periodic supercell calculation with cell dimensions of 19.494 Å x 28 Å x 20.828 Å. The longest cell dimension indicates the non-periodic direction. Energy-minimized binding configurations were explored with the N3 dye attached to ZnO through different numbers of carboxylic and thiocyanate groups. Since the time-resolved XPS measurements were performed under ultra-high vacuum conditions, the structural optimizations were carried out without including any solvent. The bonding motif calculations were performed using the VASP¹⁶ package, which employs projector augmented wave (PAW)¹⁷ pseudopotentials in conjunction with a plane-wave basis set. The generalized gradient approximation to the exchange correlation functional in the PBE¹⁸ form was used. A plane-wave cutoff of 350 eV and pseudopotentials with the following valence electronic configurations were employed: Zn(3d¹⁰4s²), O(2s²2p⁴), C(2s²2p²), N(2s²2p³), S(3s²3p⁴), H(1s¹), Ru(5s¹4d⁷). The Brillouin zone was sampled at the Γ point. Structures were optimized until all the forces were less than 0.04 eV/Å. Four different bonding motifs studied are shown in Fig. S6. We find that chemisorption of N3 on ZnO occurs primarily through the carboxylic groups on the dicarboxylic-bipyridine (dcbpy) ligands whereby the COO⁻ moiety binds to Zn sites in a Zn-O-C-O-Zn geometry while the H⁺ ions detached from the COO⁻ groups bind to a nearest neighbor O site on the ZnO surface. In general, the total energy of the system is found to be lowered with increasing number of

carboxylate groups bound to the ZnO surface. In the most stable configuration that was identified (Fig. S6a), three COO^- groups are attached to ZnO, two of them in a Zn-O-C-O-Zn geometry and the third in a Zn-O-C-O---H-O geometry in which the O---H bond indicates hydrogen bonding. The next higher energy structure identified is separated by ~ 1.28 eV in energy and is therefore thermodynamically strongly disfavored. We find that binding to ZnO through the thiocyanate (N-C-S) moiety at the expense of a carboxylate bond is not energetically favorable (Figs. S6b,d).

In order to model the electronic excited states and associated core-level shifts, a cluster model of N3-ZnO was built from the lowest energy configuration identified in the supercell calculations. As shown in Fig. S7, this configuration consists of the N3 dye chemisorbed onto a 150 atom cluster of ZnO. The geometry of the cluster was re-optimized using the VASP code. The choice of a cluster model is based on computational feasibility considerations related to the use of hybrid-DFT¹⁹ functionals.¹⁹ The N3-ZnO periodic slab model consists of 347 atoms and 1000 electrons, which is currently prohibitively expensive to model using hybrid functionals within a plane-wave basis set and a periodic supercell approach. Hybrid-DFT is more tractable for the smaller N3-ZnO cluster when modeled using a Gaussian orbital basis set and an open boundary condition framework.

S5.2 Solvated and *in vacuo* N3 dyes

Before we present the results for the photoexcited N3-ZnO cluster model, it is useful to discuss the excitation energies of an individual N3 dye molecule in its solvated state and in vacuum. This serves to benchmark our calculations against previously published results. The excited state energies and associated Ru-3d core-level shifts (ΔE_b) were calculated using the NWChem²⁰ code.²⁰ Ru was modeled using the Sapporo-DZP-2012²¹ all-electron basis set while N, C, S, Zn and O were modeled using the SBKJC²²⁻²³ basis-set and associated effective core potential (ECP). H was described through the 6-311+G* basis-set. Ru 3d core-level shifts ΔE_b are estimated using the initial state rule to calculate differences in core-level eigenvalues of ground and valence excited states. Linear-response time dependent density functional theory²⁴ (TDDFT) calculations were carried out within the Tamm-Dancoff approximation.²⁵ Structural optimizations on the solvated and *in vacuo* dye molecules were carried out at the B3LYP²⁶⁻²⁷ level. The solvated form of the dye is simulated using the COSMO²⁸ solvation model with water as solvent. In this

configuration, the dcbpy ligands are assumed to be fully deprotonated and the solvent acts to stabilize the negatively charged COO^- groups on the dcbpy ligands. This model is the same as the one employed previously by Van Kuiken *et al.*²⁹ In the *in vacuo* configuration of the dye, the COO^- groups on the dcbpy ligands are protonated and the molecule has neutral charge. We find that the geometry around the Ru site is very similar in the solvated and *in vacuo* dyes, with the Ru-N bond distances in the former case, at 2.072 Å, being 0.1% longer. Meanwhile the thiocyanate C-S bond is shorter by ~3% in the solvated dye relative to the *in vacuo* dye.

Calculated excitation energies and associated core-level shifts corresponding to the lowest singlet and triplet metal-to-ligand charge transfer (MLCT) states on the N3 dye are listed in Table S2. We focus on these states because of their importance in the photoinduced dye-substrate electron-injection process. The energies of the optically allowed singlet ($^1\text{MLCT}$) and the optically forbidden triplet ($^3\text{MLCT}$) excitations are estimated from TDDFT with three different exchange-correlation (XC) functionals *viz.*, BLYP,³⁰⁻³¹ B3LYP,²⁶⁻²⁷ and CAM-B3LYP,³² featuring increasing proportions of Hartree-Fock exchange. The $^3\text{MLCT}$ state is also modeled separately in a ΔSCF sense, as the lowest self-consistent field solution with a total spin of $S=1$. From this, the Ru 3d core-level shifts relative to the ground state are extracted. Unless explicitly indicated, all quantities in the following discussion refer to B3LYP estimates.

The main observation from Table S2 is that irrespective of the functional used, the MLCT excitation energies as well as corresponding Ru 3d core-level shifts on the *in vacuo* dye are significantly smaller than those on the solvated dye. The effect of solvation on excitation energies of the N3 dye has been investigated previously by Fantacci *et al.* who reported the same trend.³³ We note that the Ru 3d ΔE_b of -1.56 eV for the $^3\text{MLCT}$ excitation in the solvated dye agrees well with previous estimates for the Ru 2p ΔE_b by Van Kuiken *et al.*²⁹ The same behavior is also expected in the case of the optically allowed $^1\text{MLCT}$ excitation.

Based on Table S2, we make the following observations. Both the calculated MLCT excitation energies and core-level shifts increase in magnitude with increasing fraction of HF exchange employed within the XC functional. Secondly, the vertical excitation energies for the lowest $^3\text{MLCT}$ state estimated from TDDFT and ΔSCF compare well. Also, as one might expect, the $^3\text{MLCT}$ excitation is slightly lower in energy than the corresponding $^1\text{MLCT}$ excitation. The difference between the vertical and adiabatic excitation energies in the gas-phase calculations is

small at approximately 0.1 eV. In the solvated phase, the two sets of energies differ by a larger amount especially for the B3LYP and CAM-B3LYP functionals. This is due to the fact that in the solution phase Δ SCF calculations, the screening due to the solvent is overestimated as the frequency dependence of the solvent polarizability is not taken into account. The static dielectric constant of water $\epsilon_s=78.39$ is used to screen both the ground and excited states which will result in the excitation being over-screened, as the time-scale of optical excitations is much faster than the ~ 1 picosecond dielectric relaxation time in water.³⁴ In contrast, in the solution phase TDDFT calculations, solvent-polarized ground state orbitals and eigenvalues are employed but solvent contributions to screening in the excited state is not included. We estimate that including screening due to the high-frequency dielectric response of water characterized by $\epsilon_\infty=1.776$ would reduce the solvated excitation energies by approximately 0.04 eV, which is irrelevant for the present study.

S5.3 Dependence on XC functional

Next we comment on the relative accuracy of the different functionals represented within Table S2 in describing the N3/ZnO system. The optical absorption spectrum of solvated N3 dyes has been investigated previously and the B3LYP functional has been shown to provide a good match with experiments while pure GGAs such as BLYP slightly underestimate the excitation energies.^{33,35-37} With B3LYP, the optically allowed lowest ¹MLCT excitation on the solvated dye occurs at ~ 2.1 eV, close to the experimentally observed first absorption maximum at ~ 2.3 eV³⁸ in the N3 dye. The same excitation is predicted at 2.90 eV with CAM-B3LYP, which is well above the observed first absorption maximum. On the *in vacuo* dye, both the ¹MLCT and ³MLCT excitation energies are predicted to lie well below the energy of 535 nm photons irrespective of the XC functional. Thus we expect that when the *in vacuo* dye is excited using a 535 nm pump signal, the excitation that is accessed is well above the first ¹MLCT state.

For an isolated ZnO cluster identical to the one used to model the N3/ZnO interface, but with no dye adsorbed onto its surface, we find the Kohn-Sham bandgap to be 1.43 eV, 3.15 eV and 5.8 eV within BLYP, B3LYP and CAM-B3LYP respectively. It is well known that semi-local GGAs severely underestimate the bandgap in ZnO and earlier studies³⁹⁻⁴⁰ have employed

hybrid-DFT functionals with a fraction of HF exchange in the range of 20-25% in order to correct the bandgap and dielectric constant in ZnO. The B3LYP functional in particular, predicts a bandgap of $\sim 3.3\text{-}3.5\text{ eV}^{39,41}$ in bulk ZnO, which compares well with experimental values ($\sim 3.3\text{-}3.4\text{ eV}^{42-43}$). Expectedly, the semi-local functional BLYP underestimates the bandgap while CAM-B3LYP, which includes 65% HF exchange in the long-range significantly overestimates the same. Thus, B3LYP represents a good compromise for estimating valence electronic properties on both the dye molecule and the ZnO substrate.

S5.4. N3/ZnO interface: Electronic properties

In the following, we present the electronic properties of the N3/ZnO interface and compare them to those of an isolated *in vacuo* N3 dye molecule. For the sake of consistency, we optimized the geometry of an isolated N3 dye molecule in its ground state, within the same numerical framework as the structure of the N3/ZnO system (plane-wave DFT using VASP). In Table S3, we present the calculated electronic excitation energies and associated Ru 3d core-level shifts relative to the ground state, for an isolated N3 dye molecule and the N3/ZnO cluster. The reported quantities correspond to vertical excitations.

Three different excited states are modeled, each representing a different length scale for the charge separation in the photoexcited electron-hole pair. The first is an intra-molecular excitation on the dye analogous to the $^3\text{MLCT}$ excitation wherein the electron and hole wavefunctions are essentially confined to the dye molecule. This state is modeled by constraining the total spin population on the N3/ZnO cluster to two un-paired electrons, representing a spin state of $S=1$. Additionally, the total number of electrons on the dye molecule, as given by a Lowdin population,⁴⁴ is constrained to be the same as in the ground state. In other words, the constraint acts to confine the excited electron density to the adsorbed molecule and prevents partial delocalization onto the ZnO nanoparticle. This configuration represents the limiting case of an intra-molecular excitation. For this we employ the constrained density functional theory (CDFT) formalism due to Van Voorhis *et al.*⁴⁵

The second excited state represents a charge-transfer (CT) state in which the electron has been transferred to the ZnO substrate while the hole is confined to the adsorbed N3 dye. The

average separation between the electron and hole wavefunctions in this case is longer than in the $^3\text{MLCT}$ state and mimics the nature of an interfacial complex proposed previously.⁴⁶⁻⁴⁸ The CT state is also modeled using CDFT. Here, the applied constraint is such that relative to the ground state, there is one less electron on the N3 dye and one more electron on the ZnO substrate in the CT state, the total number of electrons in the N3/ZnO system remaining the same. The interfacial CT state is modeled explicitly as a charge-separated state with the N3 dye acting as the donor and the ZnO nanoparticle acting as the acceptor. In using CDFT to describe this state, we circumvent the limitations⁴⁹ of standard hybrid-DFT¹⁹ functionals in describing charge-transfer excitations within linear-response time-dependent DFT.²⁴ The effect of the $1/R$ electron-hole attraction is self-consistently included in the CDFT description.⁴⁵

The third excited state is one in which the excited electron and hole are infinitely far apart and represents an oxidized or fully ionized (FI) configuration of the chemisorbed N3 dye. This state is simulated by removing one electron from the neutral N3/ZnO system whereby the Kohn-Sham orbital that is emptied resembles the HOMO orbital on the N3 molecule. A Lowdin population analysis confirms that the electronic population over the dye molecule is reduced by one while the population on the ZnO substrate is virtually unchanged. The energy of this state relative to the ground state therefore represents the ionization potential for the adsorbed dye. By comparing the excitation energies common to both the isolated N3 dye and the N3/ZnO cluster, we see that the $^3\text{MLCT}$ state is weakly affected by the presence of the ZnO substrate. In contrast, both the excitation energy and the associated Ru-3d core-level shifts ΔE_b of the oxidized (FI) state are systematically lowered in the N3/ZnO system due to the image-charge polarization effect.⁵⁰

The calculated Ru 3d core-level shifts in the N3/ZnO cluster show the same trend as in the isolated N3 molecule with increasing proportion of HF exchange (HFX) in the XC functional. For example, the semi-local BLYP that includes no HFX, typically overestimates charge screening effects, leading to an underestimate of the chemical shift in the dye-semiconductor system. In contrast, the CAM-B3LYP functional, which includes 65% HFX in the long range, underestimates intermediate to long range screening in the N3-ZnO system as evidenced by its significant overestimation of both the optical absorption onset in the N3 dye and the band gap in ZnO (see Table S2 and section S5.3 above). The under-screening of valence excitations within CAM-B3LYP likely leads to an overestimation of the core-level shifts associated with the

valence excitations. Therefore, the ΔE_b predicted by CAM-B3LYP represent a reasonable upper-bound. In spite of this dependence upon the XC functional, the predicted ranges of Ru-3d core-level shifts corresponding to the $^3\text{MLCT}$, CT and FI states are sufficiently separated to strongly favor only the CT state based on the experimental results (Fig. 4 in main article). We find that the $^3\text{MLCT}$ state is associated with a ΔE_b that is systematically too low compared to the experimentally observed ΔE_b . Meanwhile the FI state has a ΔE_b that is too high irrespective of the DFT functional approximation. The various predicted Ru-3d core-level shifts for the CT state straddle the experimental result with the B3LYP value lying close to it. Thus, we infer that the length scale of charge separation between the photoexcited electron and hole in the N3/ZnO system at the sub-picosecond timescale is commensurate with an interfacial complex.

Fig. S6. Four different bonding motifs of N3 on ZnO ($10\bar{1}0$) in order of increasing relative energy. The lowest energy configuration (a) has five COO^- oxygen atoms bonded to Zn atoms on the surface while a sixth COO^- oxygen is hydrogen bonded to an H^+ ion adsorbed on a nearby surface O site.

Fig. S7. Highest occupied molecular orbitals (HOMOs) from slab (left) and cluster (right) models of N3/ZnO. Iso-surfaces at 5% of the maximum electron densities are depicted. The character of the HOMO state is unchanged between the two models.

Functional	Solvated ΔE (eV)				<i>In vacuo</i> ΔE (eV)			
	$^1\text{MLCT}$	$^3\text{MLCT}$			$^1\text{MLCT}$	$^3\text{MLCT}$		
	TDDFT	TDDFT	ΔSCFV	ΔSCFA	TDDFT	TDDFT	ΔSCFV	ΔSCFA
BLYP	1.61	1.51	1.73 [-1.08]	1.57 [-0.96]	0.63	0.50	0.76 [-0.26]	0.63 [-0.30]
B3LYP	2.19	1.99	1.97 [-1.74]	1.72 [-1.56]	0.97	0.81	0.95 [-0.77]	0.86 [-0.79]
CAM-B3LYP	2.90	2.44	2.30 [-2.32]	1.82 [-2.10]	1.71	1.41	1.32 [-1.68]	1.25 [-1.62]

Table S2. Excitation energies relative to the ground state and associated Ru 3d core-level shifts (ΔE_b) for the singlet ($^1\text{MLCT}$) and triplet ($^3\text{MLCT}$) metal-to-ligand charge transfer (MLCT) states of the solvated and *in vacuo* N3 dye molecule. Vertical excitation energies calculated from TDDFT are compared to ΔSCF estimates. For the $^3\text{MLCT}$ state, vertical (ΔSCFV) and adiabatic (ΔSCFA) excitation energies calculated from ΔSCF are presented. In all case, the geometries used were obtained from structural optimizations carried out at the B3LYP level, irrespective of

the functional used to calculate excitation energies and core-level shifts. The Ru-3*d* core-level shifts are noted in square brackets.

	<i>In vacuo</i> N3 dye		N3/ZnO cluster		
	Δ SCFV (eV)		Δ SCFV (eV)		
	³ MLCT	Oxidized	³ MLCT	Oxidized	CT
BLYP	0.81 [-0.27]	6.43 [-3.22]	0.63 [-0.47]	5.63[-2.71]	0.99 [-1.67]
B3LYP	0.93 [-0.69]	6.73 [-3.48]	0.94 [-0.77]	5.90[-3.36]	1.16 [-2.21]
CAM-B3LYP	1.19 [-1.41]	6.84 [-4.12]	1.13[-1.39]	6.05[-4.07]	1.79 [-2.91]

Table S3. Excitation energies relative to the ground state and associated Ru 3*d* core-level shifts for various excited states of an isolated N3 molecule and an N3/ZnO cluster. The core-level shifts are given in square brackets. All reported quantities are based on vertical Δ SCF calculations.

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