

Photocatalyzed Electron Exchange between Organic Chromophores and Hematite Nanoparticles and the Role of Solid-State Charge Transport

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Supplementary Information

Description. This document contains supporting texts, figures, and tables for the main manuscript.

Table S1 shows the amount of rhodamine B sorbed by the HNPs at unadjusted pH values in methanol medium.

Table S2 details the amount of rhodamine B sorbed by the HNPs at pH 11.

Text S1 describes the transient absorption spectroscopy results obtained for RhB and RhB+HNPs at natural pH values and pH 11.

Figures S1-S4 depict the transient absorption and decay curves for 65 μM and 20 μM rhodamine B suspended with HNPs in methanol at unadjusted pH values of ~ 6.7 and ~ 3 .

Figures S5-S8 display the transient absorption and decay curves for 65 μM and 20 μM rhodamine B suspension with HNPs in methanol and water at pH 11.

Table S3 details the decay time constants obtained via global Glotaran fits for 65 μM and 20 μM rhodamine in suspension with 0.1 g/L HNPs in methanol.

Table S4 reports the decay time constants for 65 μM and 20 μM rhodamine B suspension with HNPs in methanol and water at pH 11 retrieved from global Glotaran fits.

Figure S9 displays the differences retrieved for ΔOD for 65 μM RhB with and without HNPs for all delay positions for pH 4.5, 7, 9, and 11.

Text S2 explains transient absorption spectroscopy results recorded for only hematite nanoparticles suspensions.

Figures S10 and S11 illustrate transient absorption and decay curves for 1 g/L HNPs suspended in water at pH 3 for two experiments.

Tables S1-S2

Solvent	[RhB] [μM]	pH Before	pH After	[HNP] [g/L]	[RhB] sorbed by HNPs [μM]	Sorbed RhB [μmol/m²]
Methanol	20	6.7	3	0.2	2.57±0.12	0.34±0.02
Methanol	65	6.7	3	0.1	7.14±3.50	1.90±0.93
Water	20	6.7	3.2	0.2	3.00±0.41	0.40±0.05
Water	65	6.7	3.4	0.1	4.10±0.52	1.09±0.14

Table S1. This table shows the amount of rhodamine B sorbed onto hematite nanoparticles at unadjusted pH values by 65 μM and 20 μM rhodamine B with 0.1 g/L and 0.2 g/L HNPs respectively in methanol and water

Solvent	[RhB] [μM]	pH	[HNP] [g/L]	[RhB] sorbed by HNPs [μM]	Sorbed RhB [μmol/m²]
Methanol	20	11	0.2	2.12±0.77	0.26±0.09
Methanol	65	11	0.1	7.14±3.15	1.90±0.84
Water	20	11	0.2	5.37±0.40	0.65±0.05
Water	65	11	0.1	6.69±0.42	1.78±0.11

Table S2. This table displays the amount of rhodamine B sorbed onto hematite nanoparticles at 11 by 65 μM and 20 μM rhodamine B with 0.1 g/L and 0.2 g/L HNPs respectively.

Text S1

We performed time-resolved transient absorption experiments for 65 μM and 20 μM dye samples with HNPs in both methanol and water at pH 11 and an unadjusted pH value of 3 (See SI, Figs. S1-S6, Tables S3-S4). The 20 μM RhB samples contained 0.2 g/L loadings of HNPs. In contrast, the 65 μM samples were suspended with 0.1 g/L loadings of hematite nanoparticles. We carried out triplicate measurements for each RhB dye concentration, HNPs loadings, and solvent studied at pH 11 and 3.

Unlike at the buffered pH conditions discussed below, where τ_1 values remained relatively constant after equilibration with HNP suspensions, τ_1 values changed for the RhB versus RhB+HNPs samples at pH 6.7 and pH 3, respectively (Tables S3). We attribute this to the drastic change in pH following HNPs addition which possibly plays a role in the dye's dimerization thereby affecting the dimer's excited state lifetime. The first excited state relaxation lifetime, τ_1 increases by one order of magnitude after adding HNPs at pH 3 for the 65 μM and 20 μM RhB in methanol (Tables S3). τ_1 increases by one order of magnitude for 65 μM in water but decreases by an order of magnitude for 20 μM in water after adding HNPs. For the unadjusted pH samples, we observe that τ_2 increases by $\sim 50\%$ or more in methanol but decreases by at least 28% in water when HNPs are included (see Table S3). At the unadjusted pH conditions, τ_3 increases by at least an order of magnitude for 20 μM dye in methanol, 65 μM , and 20 μM dye RhB dye concentrations in water but decreases by one order of magnitude for 65 μM dye in methanol after HNPs addition (Table S3).

After performing Glotaran analysis, we observe that τ_1 for the dye barely changes after sorption by HNPs within standard measurement error at pH 11. By taking into account standard deviation values, τ_1 values at pH 11 do not change from RhB to RhB+HNPs (Table S4). The fluorescence decay lifetime (second excited state relaxation lifetime, τ_2) decreases by $\sim 9\%$ or more following HNPs inclusion at pH 11 (Table S4). Likewise, τ_3 decreases by at least 35% after addition of HNPs at pH 11 except for 20 μM dye and 0.2 g/L HNPs suspensions in water where τ_3 relatively stays the same when uncertainty is considered after

HNPS addition (Table S4). Similarly, τ_3 decreases or remains the same when considering uncertainties while comparing RhB and RhB+HNPs at pH 11 in water and methanol (see SI, Text SI, Table S4)

Figures S1-S4

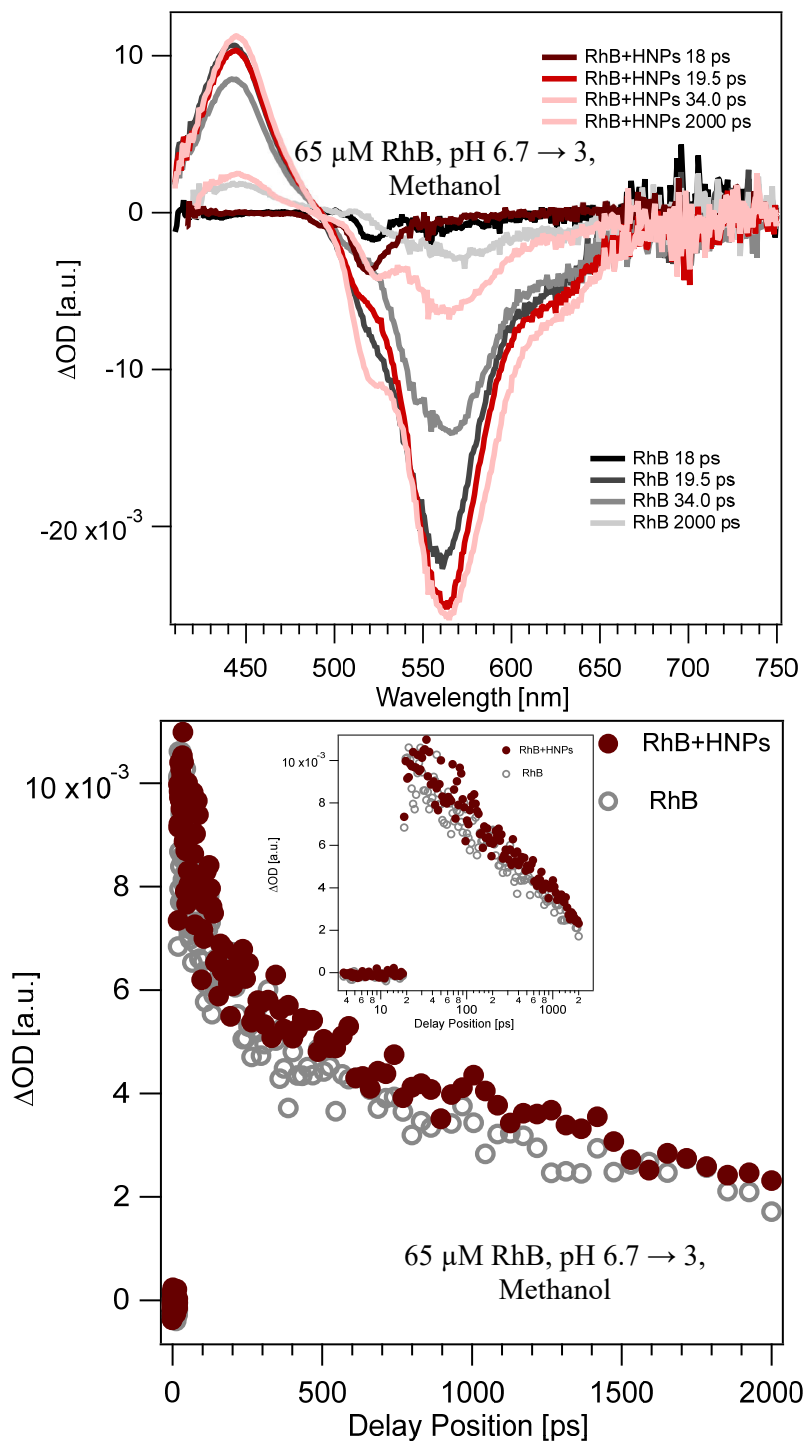


Figure S1. (Top) Transient absorption spectra for 65 μM Rhodamine B with and without 0.1 g/L hematite nanoparticles suspended in methanol at unadjusted pH values of 6.7 (RhB only) and 3 (RhB+HNPs). (Bottom) Transient absorption kinetics for 65 μM Rhodamine B with and without 0.1 g/L hematite nanoparticles in suspension in methanol medium at unadjusted pH values of 6.7 (RhB only) and 3 (RhB+HNPs) at 448 nm wavelength.

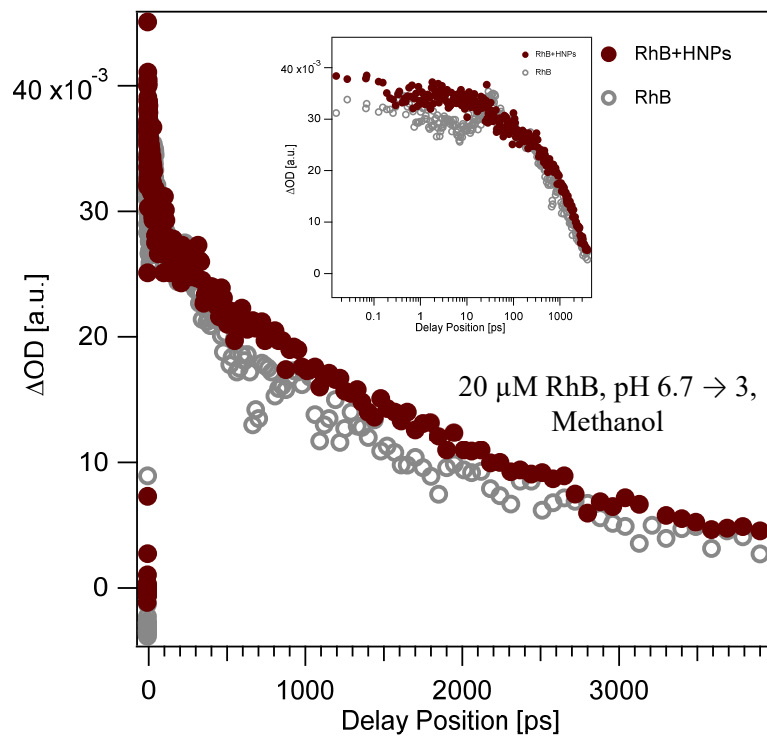
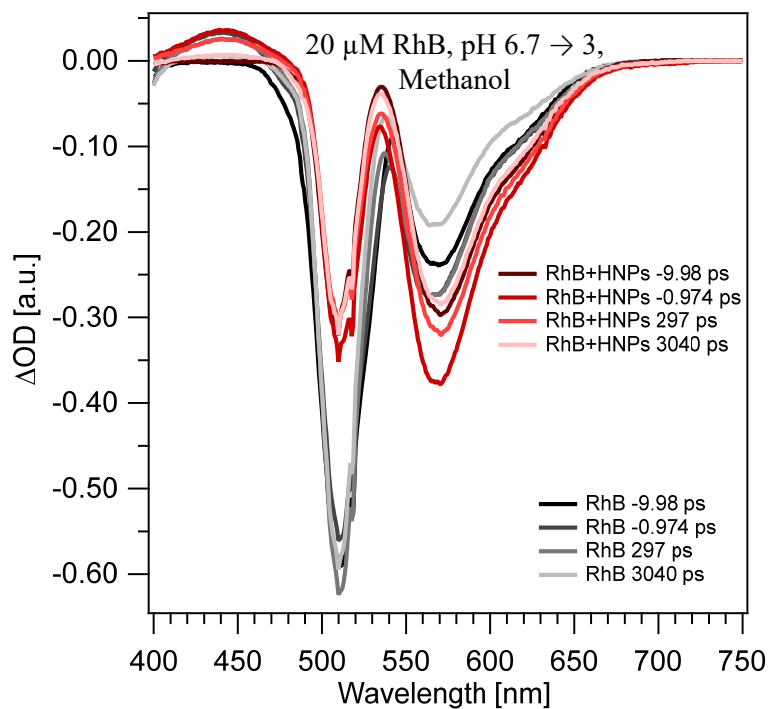


Figure S2. (Top) Transient absorption spectra for 20 μM Rhodamine B with and without 0.2 g/L hematite nanoparticles suspended in methanol at unadjusted pH values of 6.7 (RhB) and 3 (RhB+HNPs). (Bottom) Transient absorption kinetics for 20 μM Rhodamine B with and without 0.2 g/L hematite nanoparticles in suspension in methanol medium at unadjusted pH values of 6.7 (RhB only) and 3 (RhB+HNPs), at 448 nm wavelength.

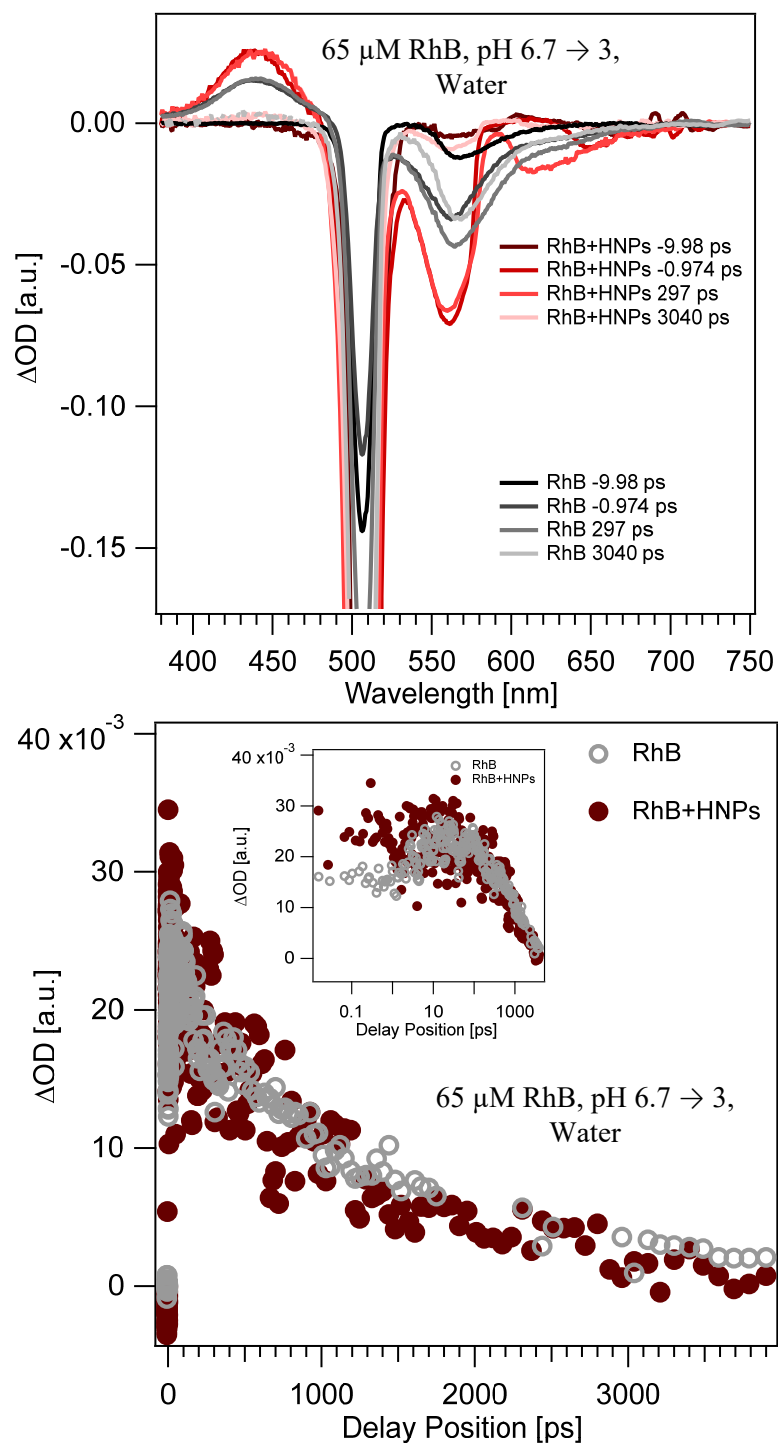


Figure S3. (Top) Transient absorption spectra for 65 μM Rhodamine B with and without 0.1 g/L hematite nanoparticles suspended in water at unadjusted pH values of 6.7 (RhB only) and 3 (RhB+HNPs). (Bottom) Transient absorption kinetics for 65 μM Rhodamine B with and without 0.1 g/L hematite nanoparticles in suspension in water medium at unadjusted pH values of 6.7 (RhB only) and 3 (RhB+HNPs) at 448 nm wavelength.

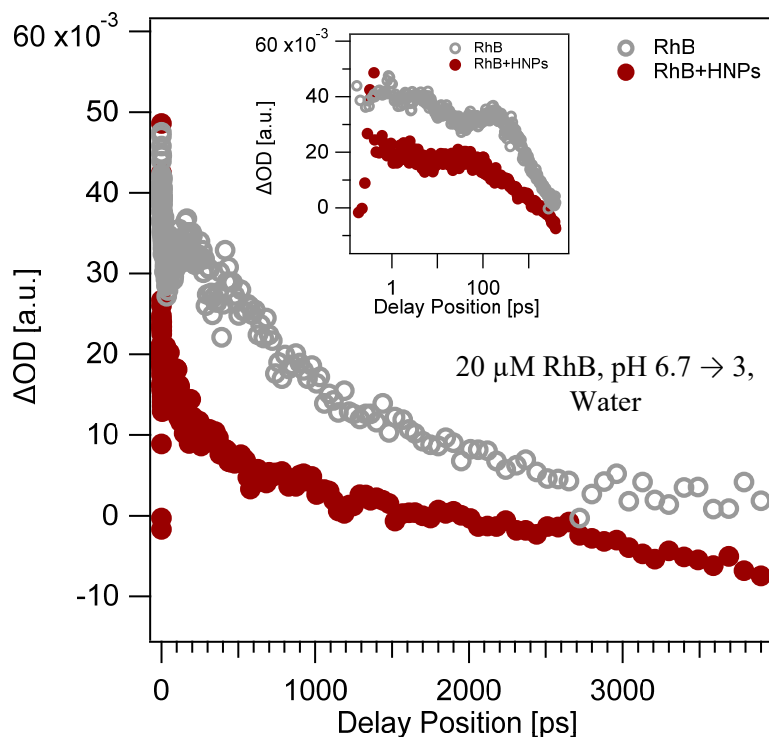
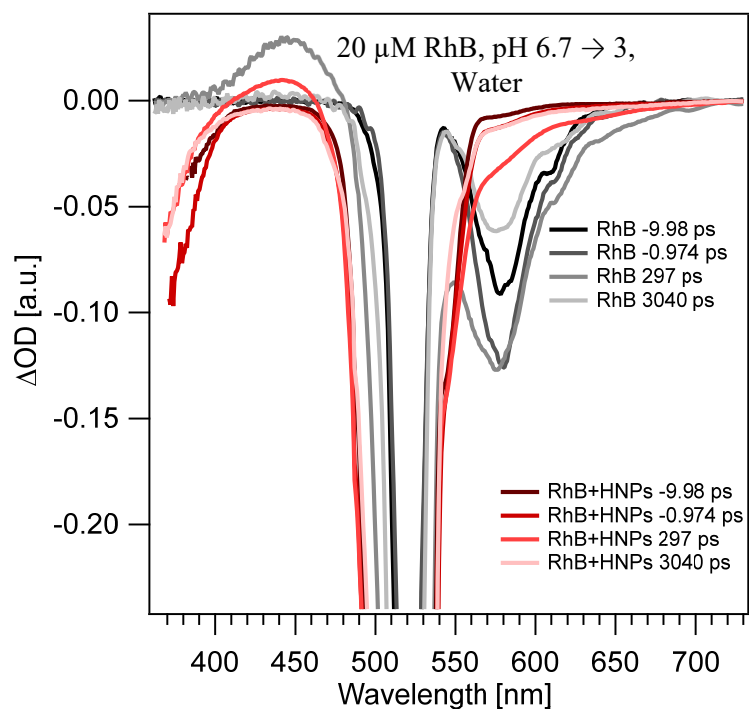


Figure S4. (Top) Transient absorption spectra for 20 μM Rhodamine B with and without 0.2 g/L hematite nanoparticles suspended in water at unadjusted pH values of 6.7 (RhB only) and 3 (RhB+HNPs). (Bottom) Transient absorption kinetics for 20 μM Rhodamine B with and without 0.2 g/L hematite nanoparticles in suspension in water medium at unadjusted pH values of 6.7 (RhB only) and 3 (RhB+HNPs) at 448 nm wavelength.

Figures S5-S8

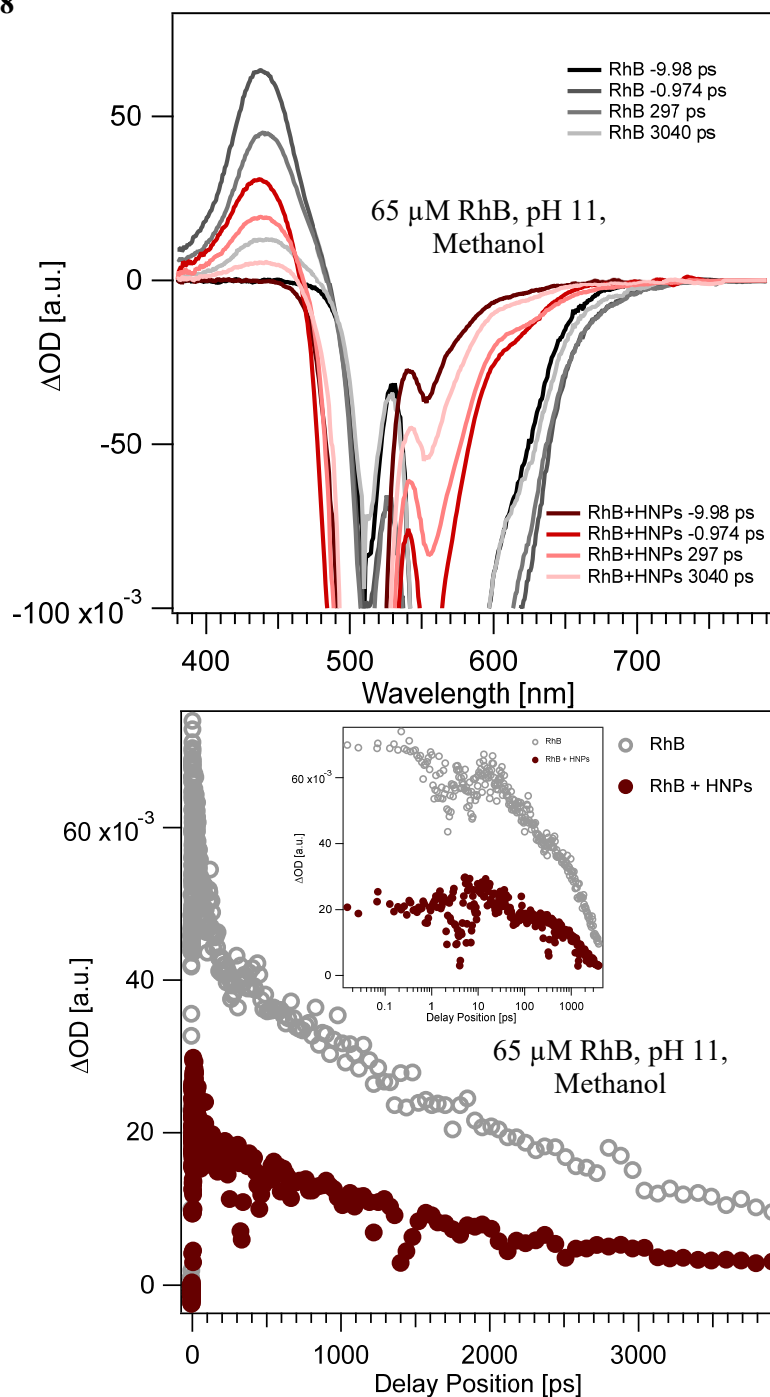


Figure S5. (Top) Transient absorption spectra for 65 μM Rhodamine B with and without 0.1 g/L hematite nanoparticles suspended in methanol at pH 11 and different delay times. (Bottom) Transient absorption kinetics for 65 μM Rhodamine B with and without 0.1 g/L hematite nanoparticles in suspension in methanol medium at pH 11 at 448 nm wavelength. To facilitate a continuity of explaining observed trends, figure S1 is the same as figure 5.

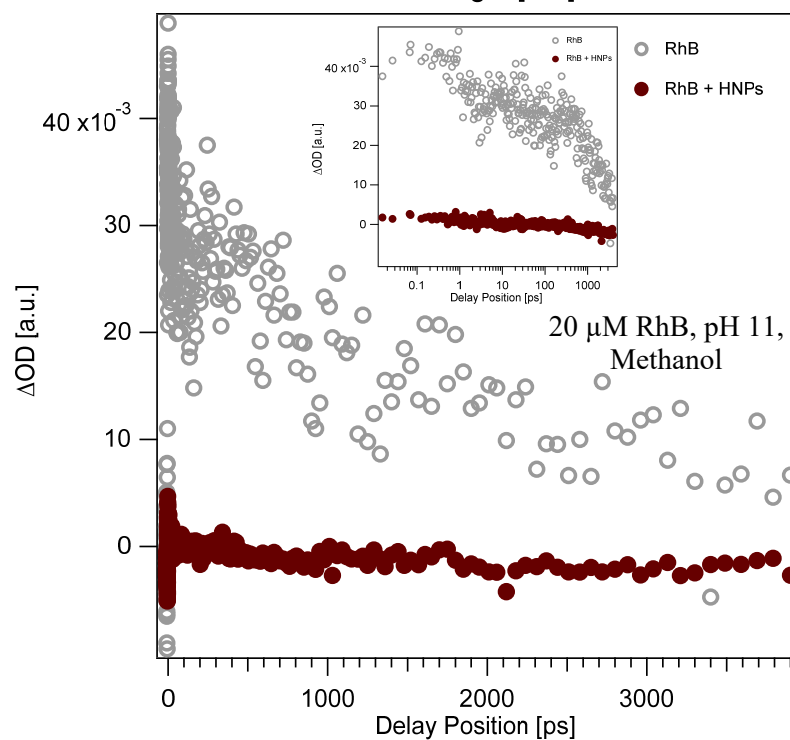
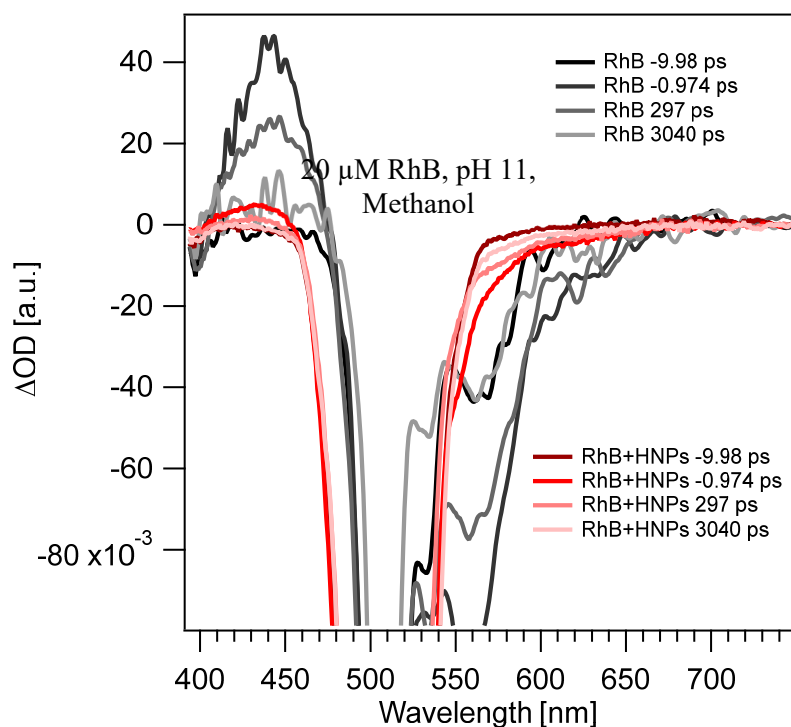


Figure S6. (Top) Transient absorption spectra for 20 μM Rhodamine B with and without 0.2 g/L hematite nanoparticles suspended in methanol at pH 11 and different delay times. (Bottom) Transient absorption kinetics for 20 μM Rhodamine B with and without 0.2 g/L hematite nanoparticles in suspension in methanol medium at pH 11 at 448 nm wavelength.

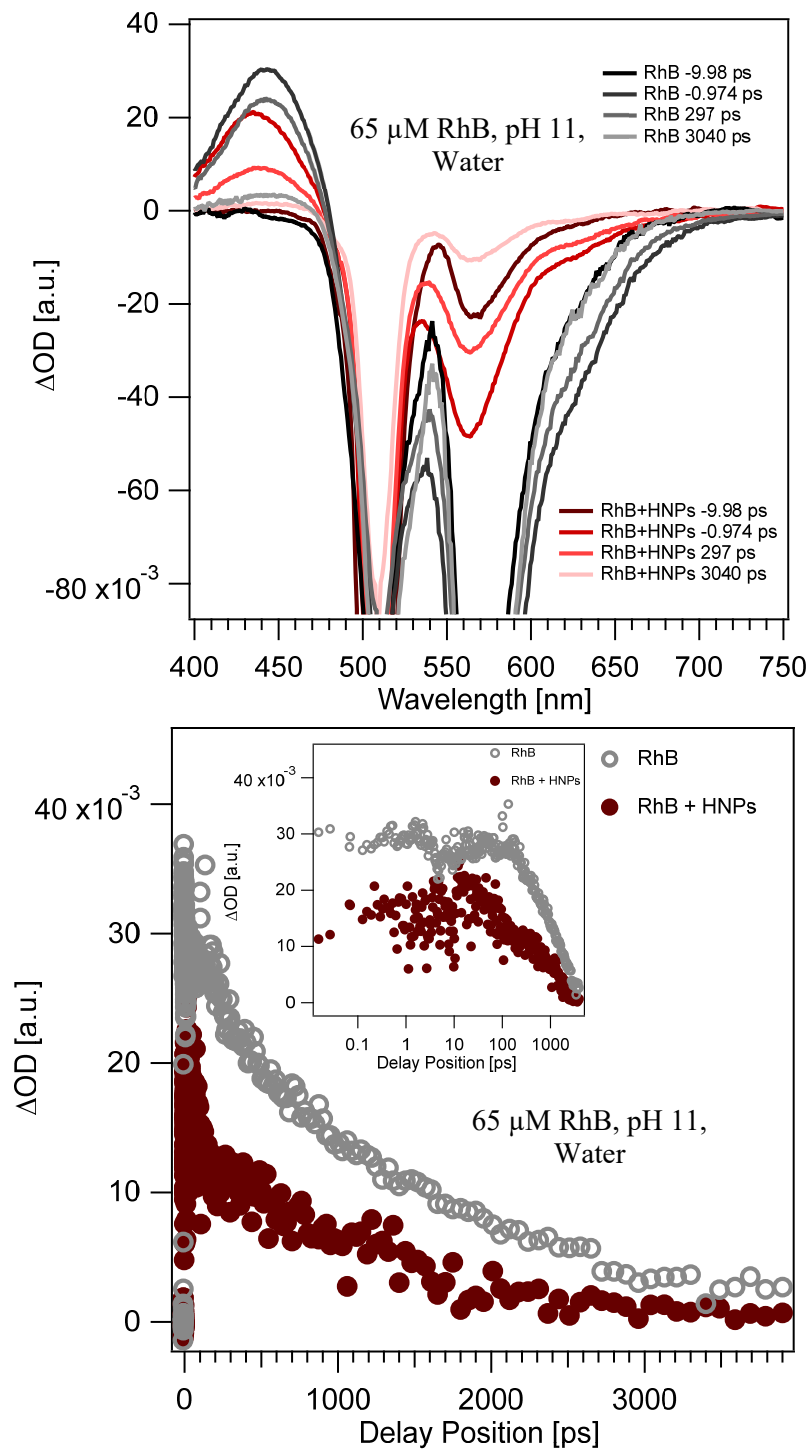


Figure S7. (Top) Transient absorption spectra for 65 μM Rhodamine B with and without 0.1 g/L hematite nanoparticles suspended in water at pH 11 and different delay times. (Bottom) Transient absorption kinetics for 65 μM Rhodamine B with and without 0.1 g/L hematite nanoparticles suspended in water at pH 11 at 448 nm wavelength.

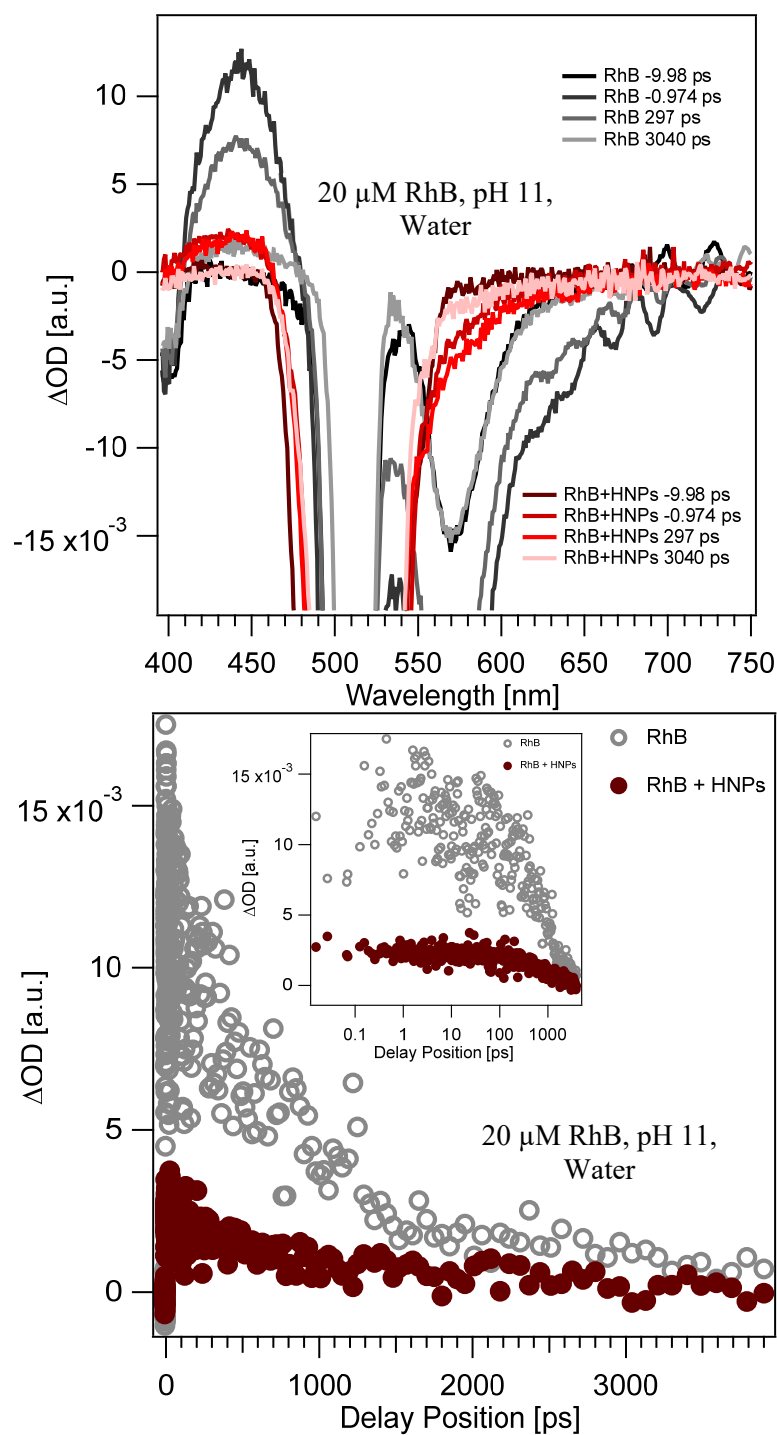


Figure S8. (Top) Transient absorption spectra for 20 μM Rhodamine B with and without 0.2 g/L hematite nanoparticles suspended in water at pH 11. (Bottom) Transient absorption kinetics for 20 μM Rhodamine B with and without 0.2 g/L hematite nanoparticles in suspension in water medium at pH 11 at 448 nm wavelength.

Tables S3-S4

Solvent	[RhB] [μM]	pH Measured	[HNP] [g/L]	τ_1 [ps]	τ_2 [ps]	τ_3 [ps]
Methanol	20	~6.7	0.0	< 63	644 \pm 124	4900 \pm 223
Methanol	20	~3	0.2	< 173	956 \pm 172	29587 \pm 773
Methanol	65	~6.7	0.0	< 18	1808 \pm 70	92973 \pm 34600
Methanol	65	~3	0.1	220 \pm 7	184000 \pm 113000	12500 \pm 584
Water	20	~6.7	0.0	< 6	2300 \pm 92	97100 \pm 4410
Water	20	~3.2	0.2	< 18	1640 \pm 65	257000 \pm 12200
Water	65	~6.7	0.0	< 115	1920 \pm 75	2620 \pm 44
Water	65	~3.4	0.1	< 11	765 \pm 53	142857 \pm 129907

Table S3. Excited state relaxation time values for RhB and RhB+HNPs suspensions with no pH adjusted.

Solvent	[RhB] [μM]	pH	[HNP] [g/L]	τ_1 [ps]	τ_2 [ps]	τ_3 [ps]
Methanol	20	11	0.0	3 \pm 3	6444 \pm 745	5442 \pm 386
Methanol	20	11	0.2	1.5 \pm 0.7	3503 \pm 209	2429 \pm 84
Methanol	65	11	0.0	6 \pm 5	5337 \pm 1901	14057 \pm 5108
Methanol	65	11	0.1	1.3 \pm 0.6	4863 \pm 1190	3433 \pm 1023
Water	20	11	0.0	21 \pm 16	4994 \pm 2362	20154 \pm 8364
Water	20	11	0.2	9 \pm 12	970 \pm 84	22722 \pm 2346
Water	65	11	0.0	12 \pm 20	1388 \pm 132	5621 \pm 554
Water	65	11	0.1	4 \pm 3	532 \pm 17	3285 \pm 82

Table S4. Excited state relaxation time values for RhB and RhB+HNPs suspensions at pH 11.

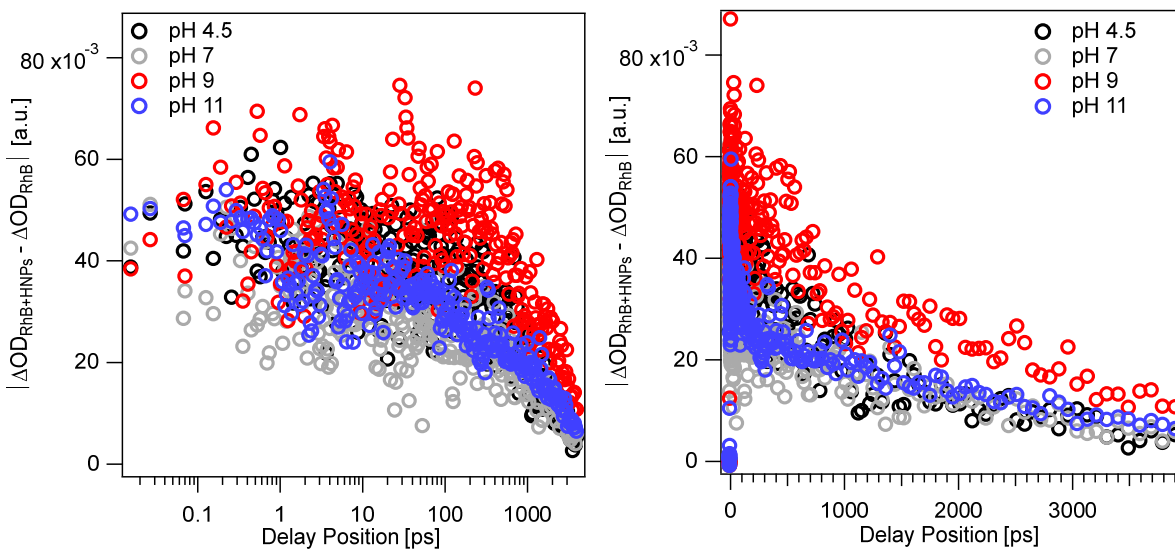


Figure S9. Difference in ΔOD derived from transient absorption kinetics for 65 μM Rhodamine B with and without 0.1 g/L hematite nanoparticles in suspension in methanol medium at pH 4, 5, 7, 9, and 11 at 448 nm wavelength. Left – Log scale, Right – Linear scale

Text S2

Transient Absorption of Hematite Nanoparticle Suspensions.

We collected transient absorption data for 0.1 g/L and 1 g/L HNPs suspended in water at pH 3 (Figs. S9-S10). Unfortunately, the transient absorption curves for 0.1 g/LHNP suspensions have no prominent positive ΔOD peaks at all wavelengths owing to a low signal-to-noise ratio. The 1 g/L HNPs suspensions show positive ΔOD peaks above ~ 550 nm, albeit ΔOD values could be only observed above 500 nm. As a result, we stick to 0.1 g/L of HNPs loading for RhB+HNPs suspensions to not cut out the positive ΔOD peak below 500 nm for RhB. Fitting the decay data of the 1 g/L HNPs suspensions to a biexponential decay curve at 600 nm yielded averaged excited-state relaxation time values of 98 ± 30 ps and 1018 ± 501 ps (see Fig. S10). The HNPs' excited state relaxation time(s) we obtained agree at least within an order of magnitude with that reported in the literature.¹ Transient absorption studies of hematite nanofilms yielded two excited-state relaxation time values of 5.7 ps and > 670 ps after fitting positive ΔOD TA kinetic curves recorded at 579 nm or 2.14 eV.¹ In their work, they point out that the ΔOD response is positive within the 2 – 2.3 eV (540 – 620 nm) using a pump wavelength of 400 nm, which is identical to the positive ΔOD region we observe above ~ 550 nm with a 515 nm pump wavelength. Negative ΔOD values or ground state bleaching peak centered around ~ 505 nm is due to absorption into impurity states in the conduction band edge.^{1,2}

Pump excitation of HNPs produces a range of electrons and holes within the valence and conduction bands of the hematite nanoplatelets. Based on previous work, the positive ΔOD values generated by the probe beam energies carry contributions from excited-state electron absorption (EA) and excited-state hole absorption (HA, i.e., hole filling), with EA being the highest contributor.²⁻⁴ Excited state electron absorption involves intra-transitions within the conduction band, whereas photogenerated holes are occupied through intra-transitions in the valence band of hematite during excited state hole absorption.¹ Therefore, the recombination of relaxed electrons (i.e., fully relaxed hot electrons in the lower conduction band of hematite) with holes is accountable for the longer lifetime values (98 ± 30 ps and 1018 ± 501 ps) we

retrieved.¹ Given these lifetime values, we would expect electrons transferred from photoexcited RhB in suspension to fill photogenerated holes in the conduction and valence bands, thus intermeddling with the EA and HA process of photoexcited hematite on similar timescales.

Figures S10-S11

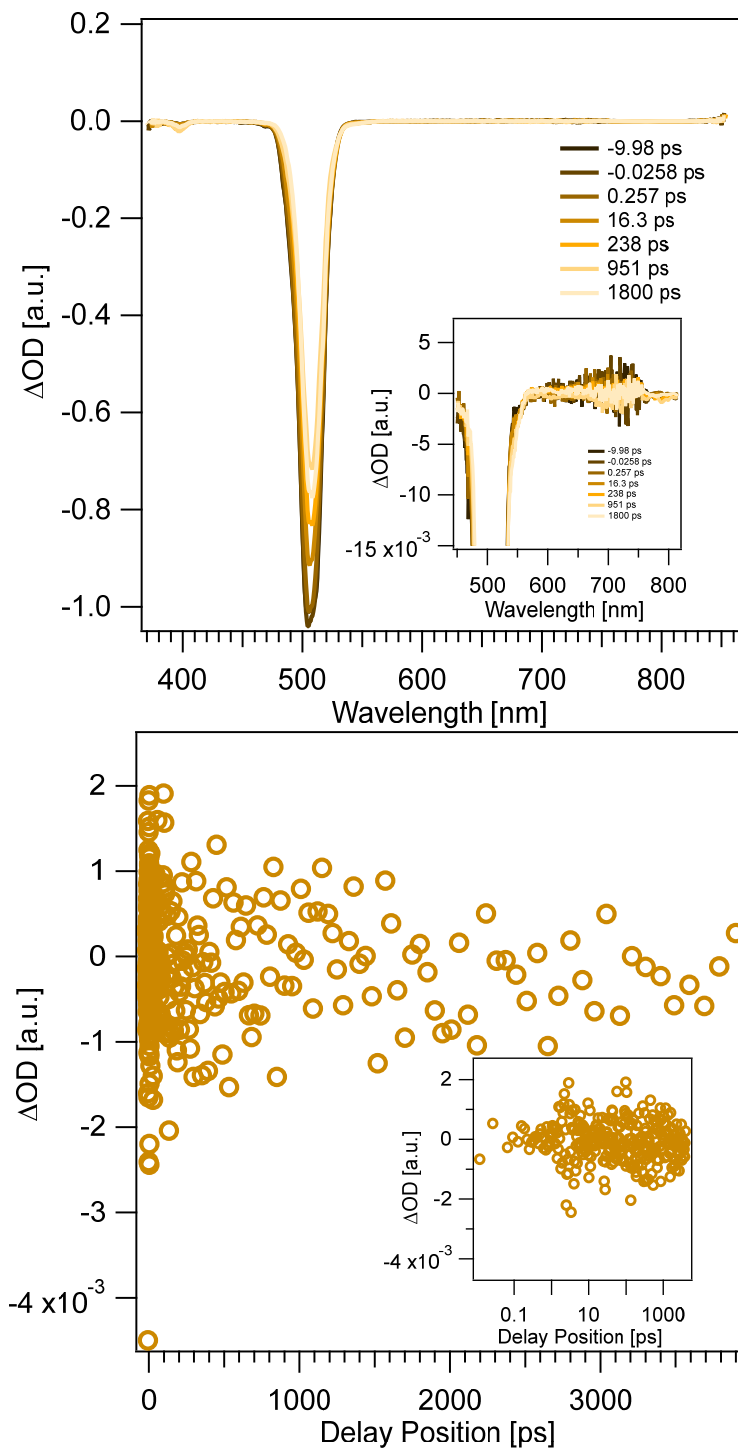


Figure S10. (Top) Transient absorption spectra for 0.1 g/L hematite nanoparticles suspended in water (Bottom) Transient absorption kinetics for 0.1 g/L hematite nanoparticles suspended in water at pH 3 at 600 nm wavelength.

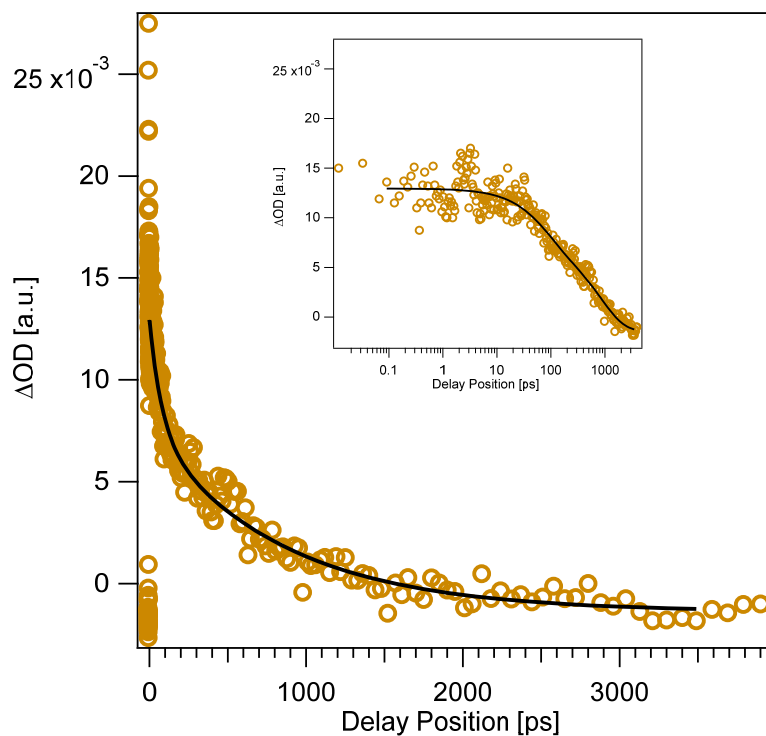
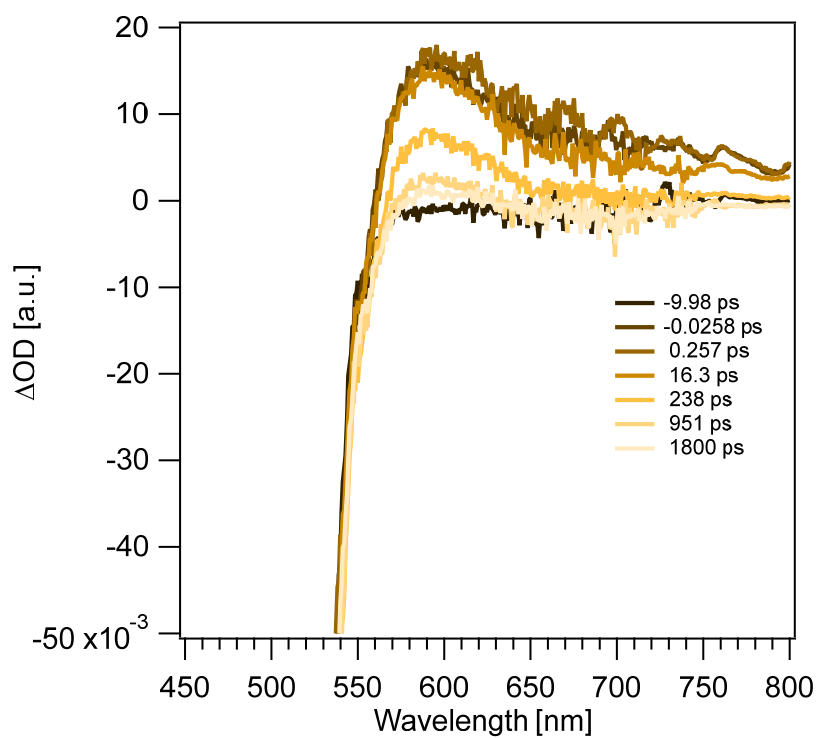


Figure S11. (Top) Transient absorption spectra for 1 g/L hematite nanoparticles suspended in water (Bottom) Transient absorption kinetics for 1 g/L hematite nanoparticles suspended in water at pH 3 at 600 nm wavelength.

Biexponential Fits for Transient Absorption Kinetics Data of Hematite Nanoparticles Suspensions.

We fitted the bottom part of Fig. S11 to a bi-exponential equation. $y = y_0 + A_1 e^{-\frac{(x-x_0)}{\tau_1}} + A_2 e^{-\frac{(x-x_0)}{\tau_2}}$ in Igor Pro software. The fit parameters are listed below:

$$y_0 = -0.0007409 \pm 0.000408, x_0 = 0.0117, A_1 = 0.0057717 \pm 0.00648, \\ A_2 = 0.0092217 \pm 0.000555 \\ \tau_1 = 79.16 \pm 16.2 \text{ ps}, \quad \tau_2 = 843.74 \pm 162 \text{ ps}$$

A duplicate experiment generated the following fit parameters:

$$y_0 = -0.0014838 \pm 0.0011, x_0 = 0.0163, A_1 = 0.0084407 \pm 0.00143, \\ A_2 = 0.0082324 \pm 0.00103 \\ \tau_1 = 116.41 \pm 26.1 \text{ ps}, \quad \tau_2 = 1192.2 \pm 540 \text{ ps}$$

References

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