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Supplementary Information

Surface Modification of Anatase Nanoparticles with Fused Ring Salicylate Type Ligands (3-hydroxy-2-naphthoic acids): A Combined DFT and Experimental Study of Optical Properties

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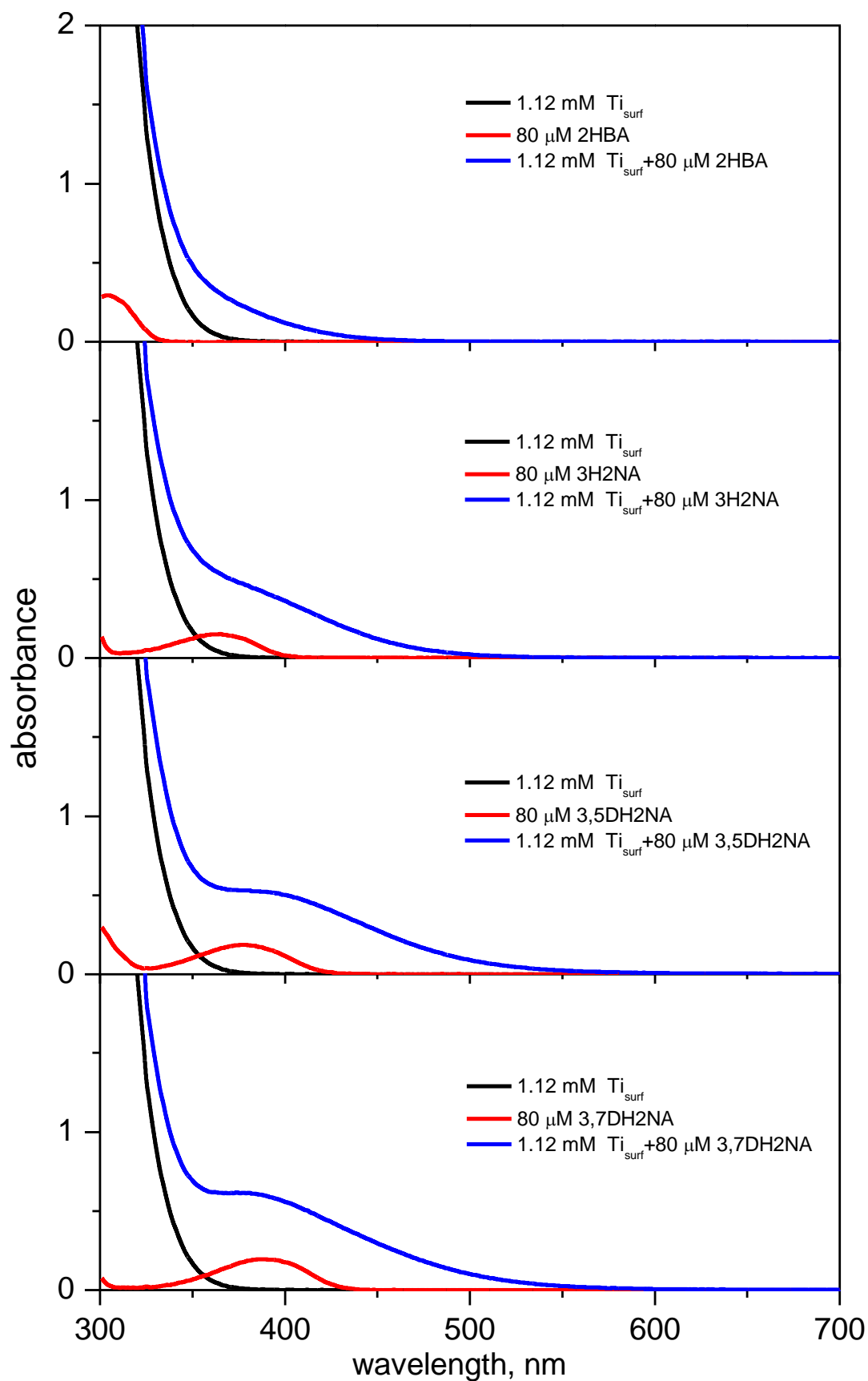


Figure SI1. Absorption spectra of TiO_2 nanoparticles (black), free ligands (red) and ligand- TiO_2 CT-complexes (blue) with 15% coverage in methanol/water=90/10, pH 2.

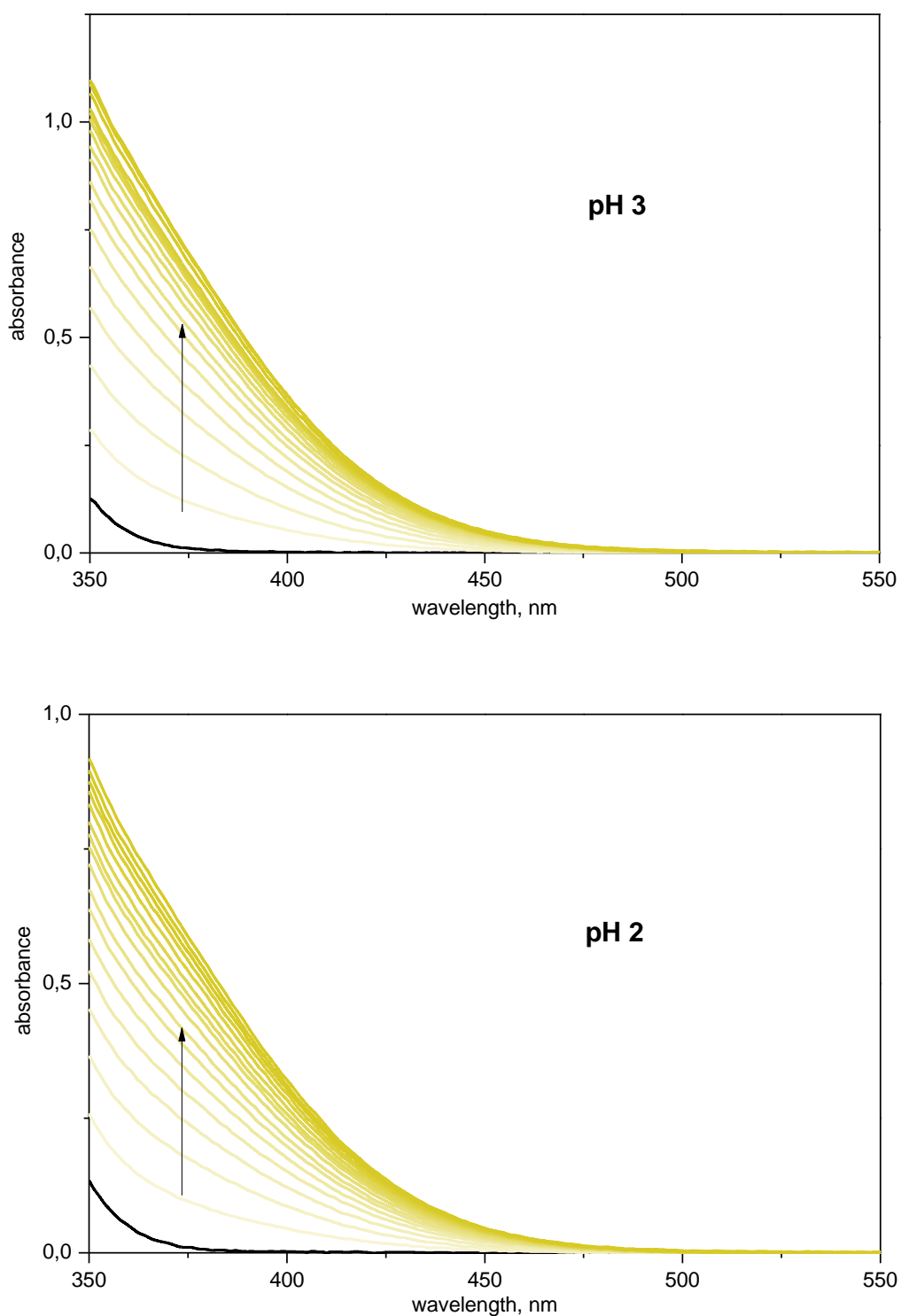


Figure S12. Absorption spectra of 3.6 mM TiO₂ (1 mM Ti_{surf}) nanoparticles before and after surface modification with 2HBA (0 – 560 μM in 35 μM steps) in methanol/water=90/10, at pH 2 and pH 3 (data recorded 20 h after surface modification).

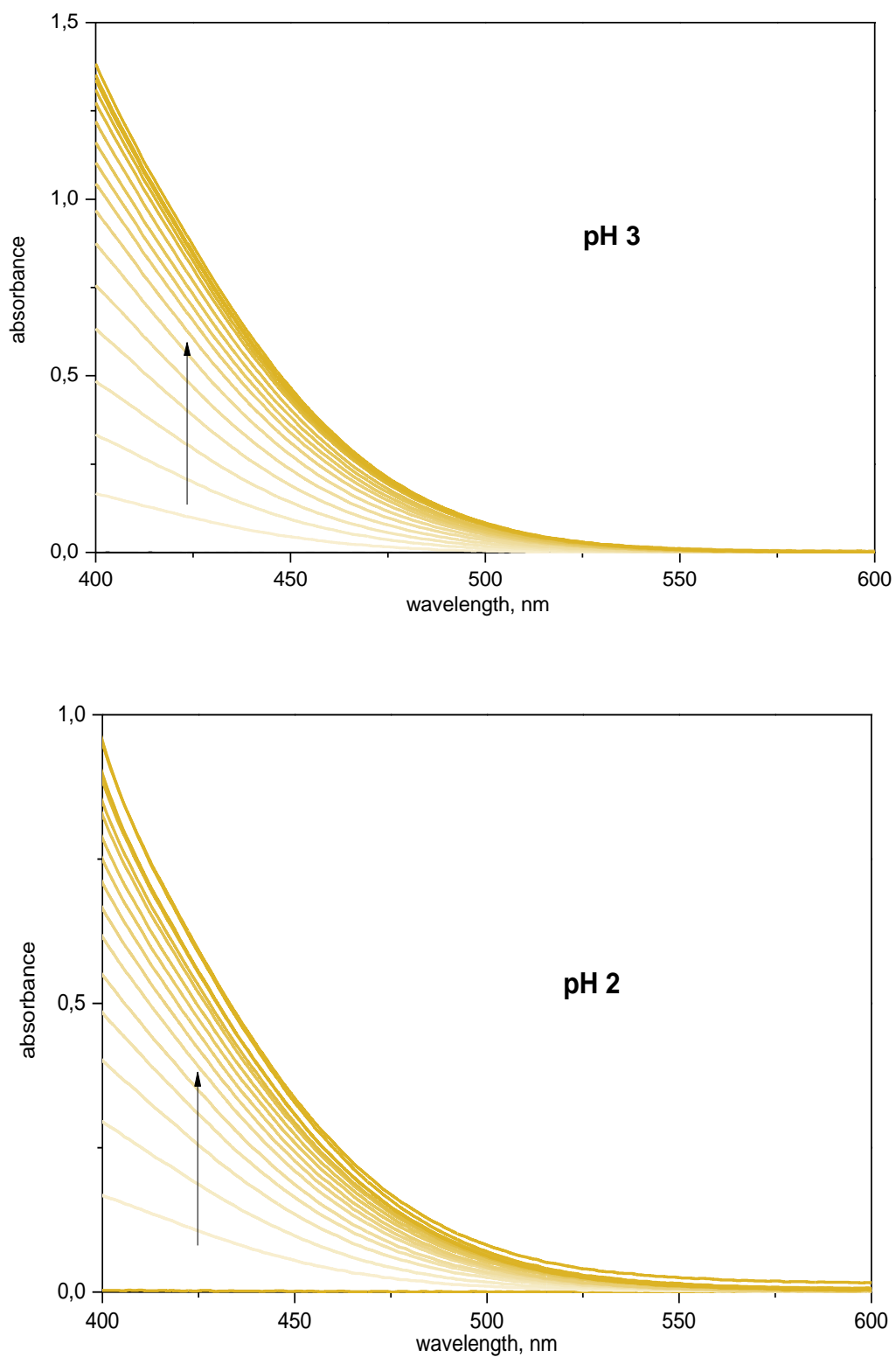


Figure S13. Absorption spectra of 3.6 mM TiO₂ (1 mM Ti_{surf}) nanoparticles before and after surface modification with 3H₂NA (0 – 560 μM in 35 μM steps) in methanol/water=90/10, at pH 2 and pH 3 (data recorded 20 h after surface modification).

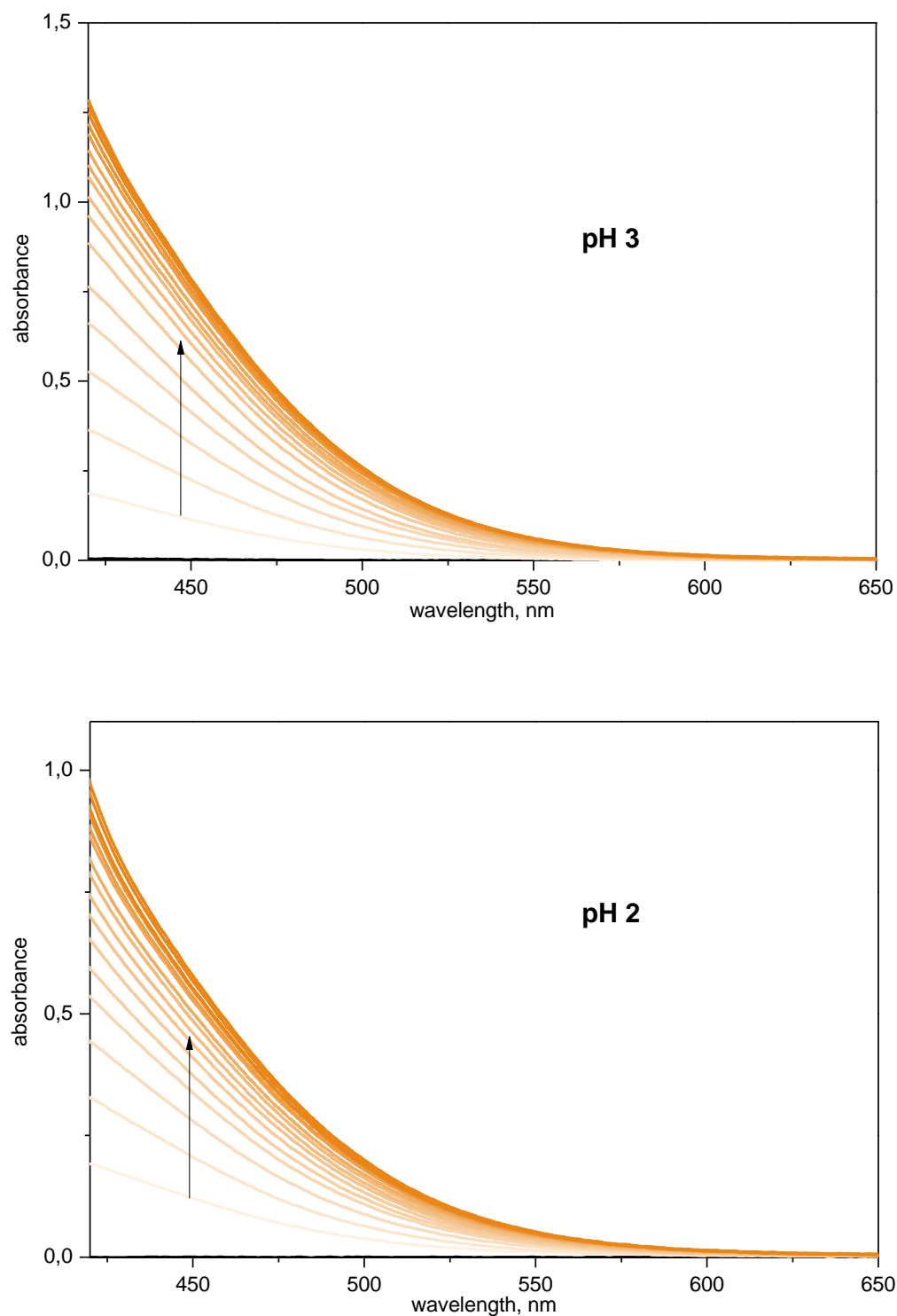


Figure SI4. Absorption spectra of 3.6 mM TiO₂ (1 mM Ti_{surf}) nanoparticles before and after surface modification with 3,5DH₂NA (0 – 560 μM in 35 μM steps) in methanol/water=90/10, at pH 2 and pH 3 (data recorded 20 h after surface modification).

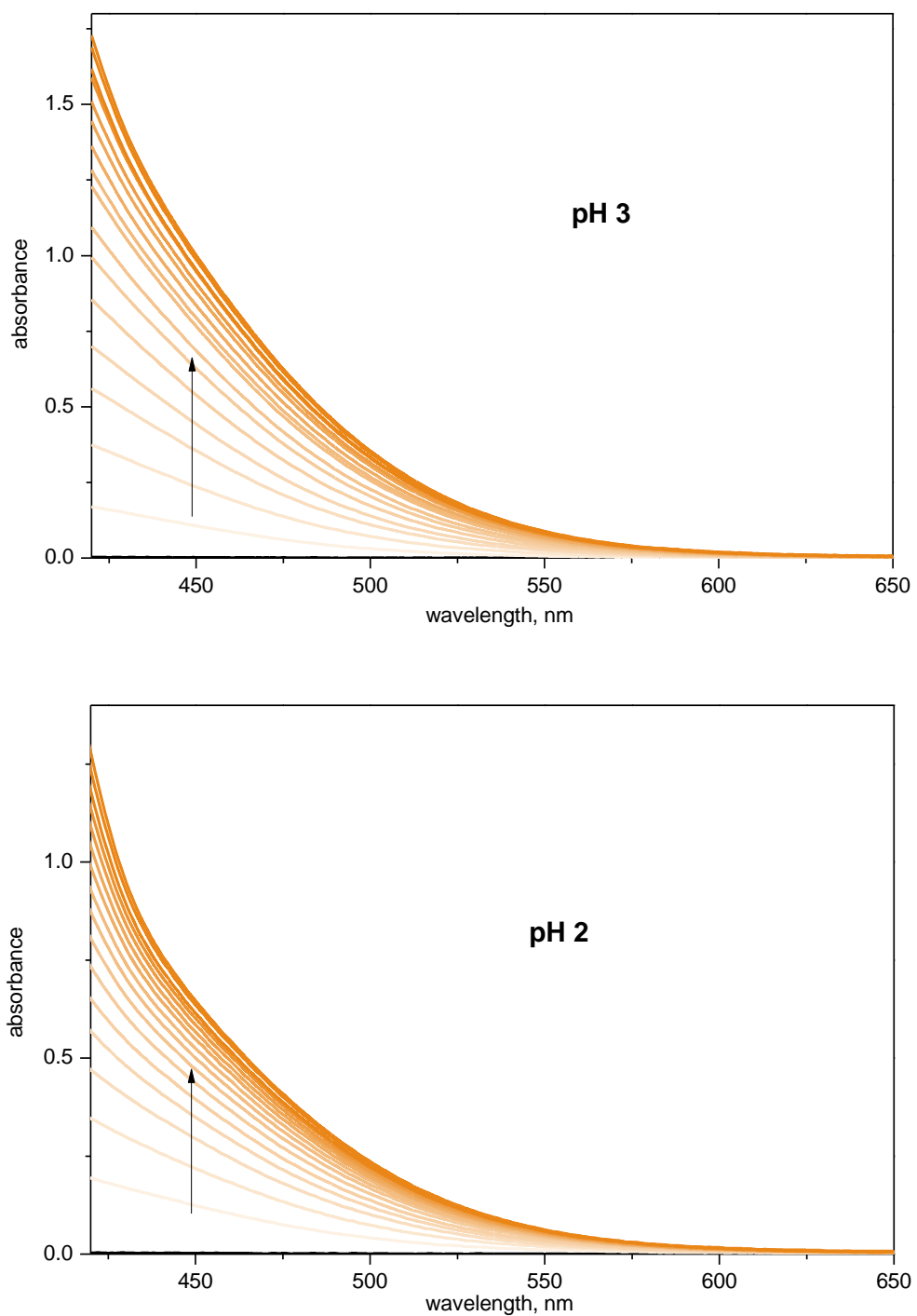


Figure SI5. Absorption spectra of 3.6 mM TiO₂ (1 mM Ti_{surf}) nanoparticles before and after surface modification with 3,7DH2NA (0 – 560 μM in 35 μM steps) in methanol/water=90/10, at pH 2 and pH 3 (data recorded 20 h after surface modification).

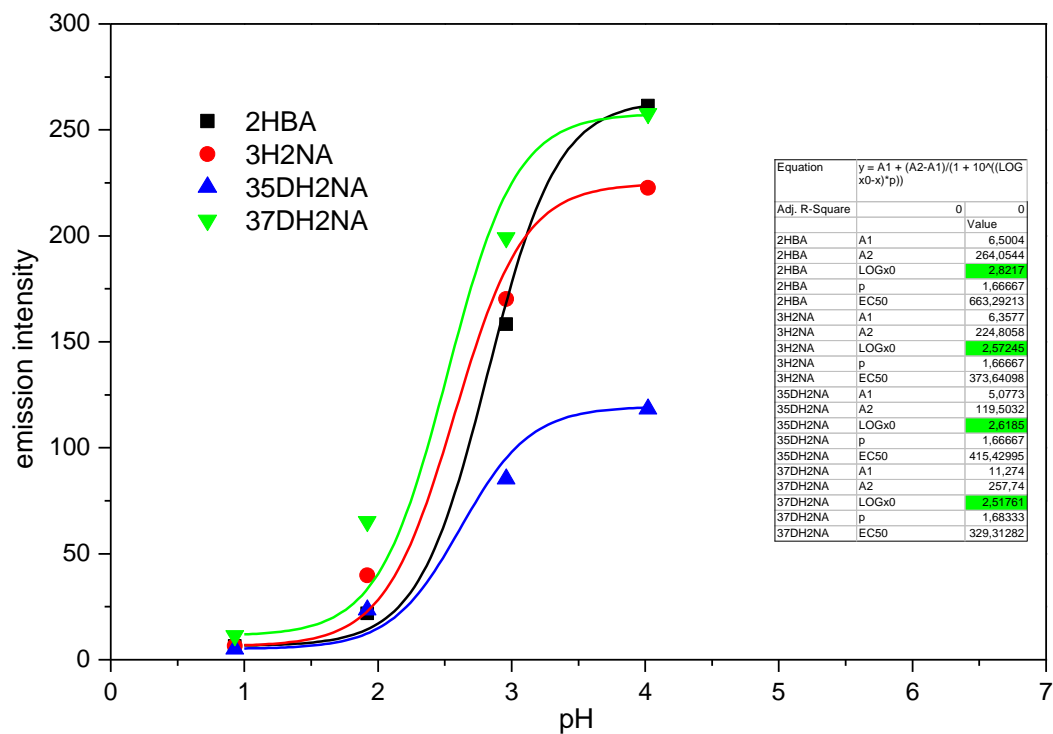


Figure S16. Fluorescence emission intensity versus pH in aqueous solution of 2HBA (2.5 μM , ex. 310 nm, em. 410 nm), 3H2NA (50 μM , ex. 360 nm, em. 520 nm), 3,5DH2NA (50 μM , ex. 370 nm, em. 530 nm) and 3,7DH2NA (50 μM , ex. 380 nm, em. 530 nm) with corresponding pK_a values (highlighted green).

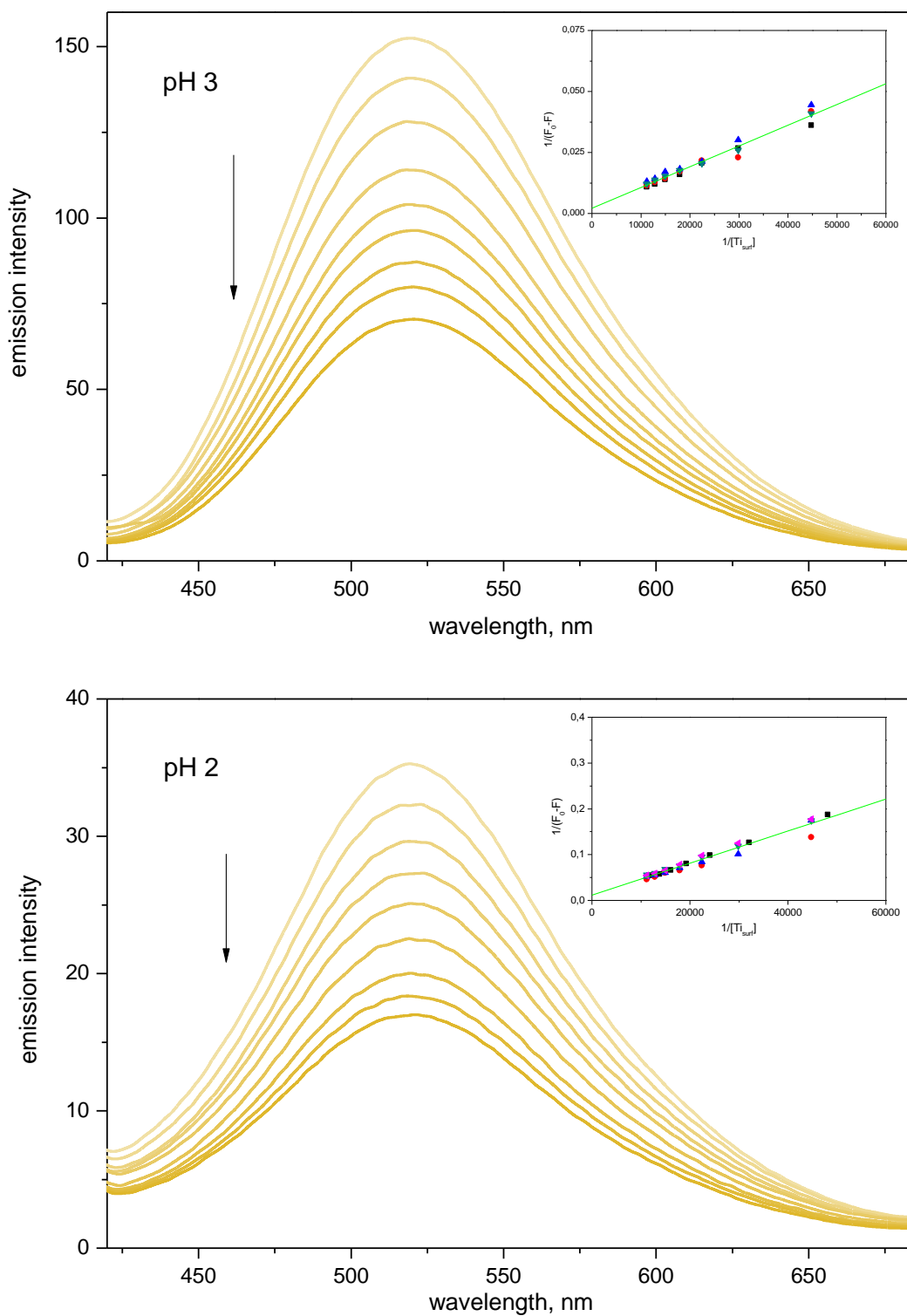


Figure S17. Emission spectra of 3H2NA (50 μ M) in the presence of various concentrations of Ti_{surf} (0-90 μ M in 10 μ M steps) in aqueous solutions, at pH 2 and pH 3 (data recorded 20 h after surface modification). Inset: Benesi-Hildebrand plot for five series of measurements.

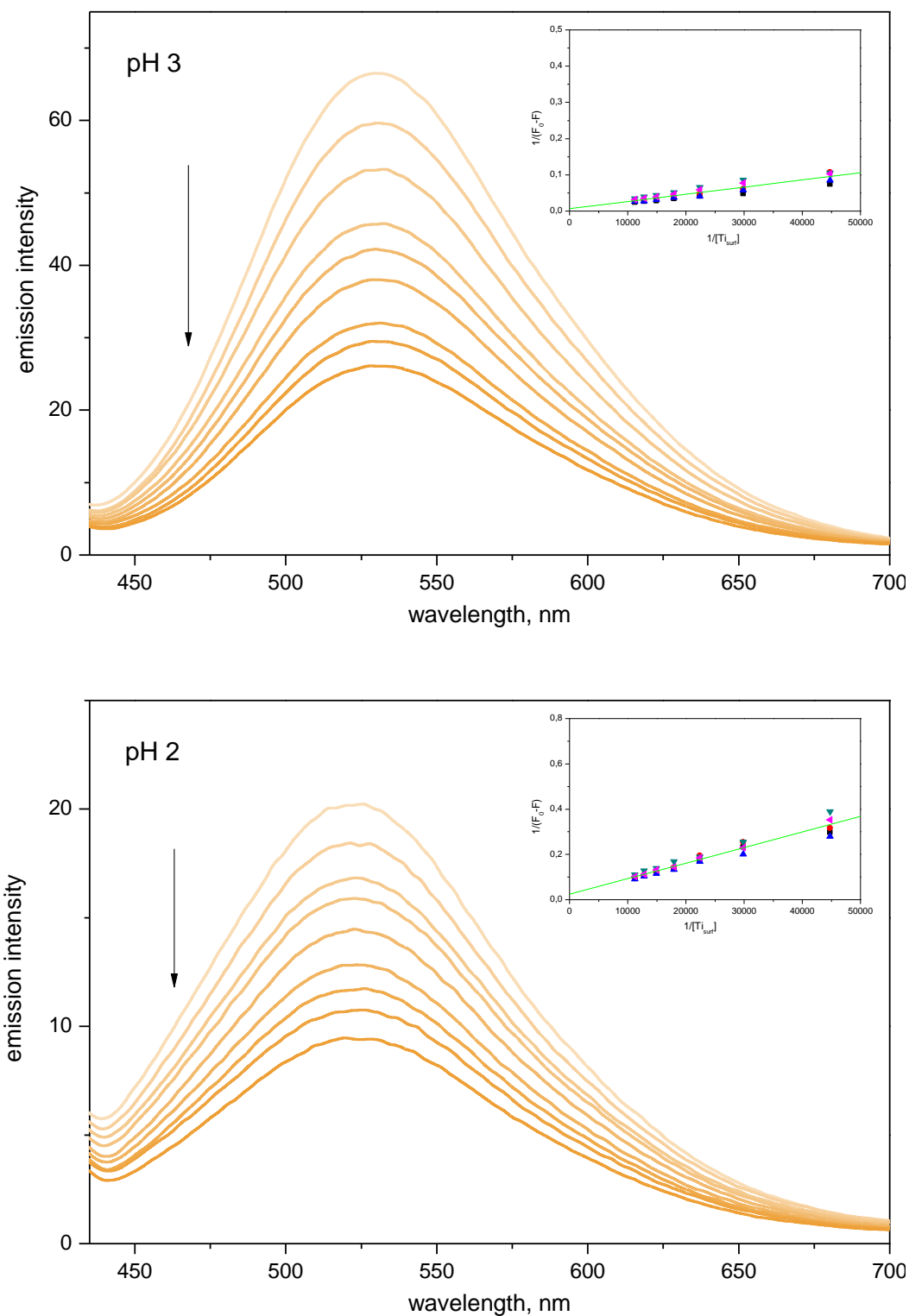


Figure S18. Emission spectra of 3,5DH2NA (50 μ M) in the presence of various concentrations of Ti_{surf} (0-90 μ M in 10 μ M steps) in aqueous solutions, at pH 2 and pH 3 (data recorded 20 h after surface modification). Inset: Benesi-Hildebrand plot for five series of measurements.

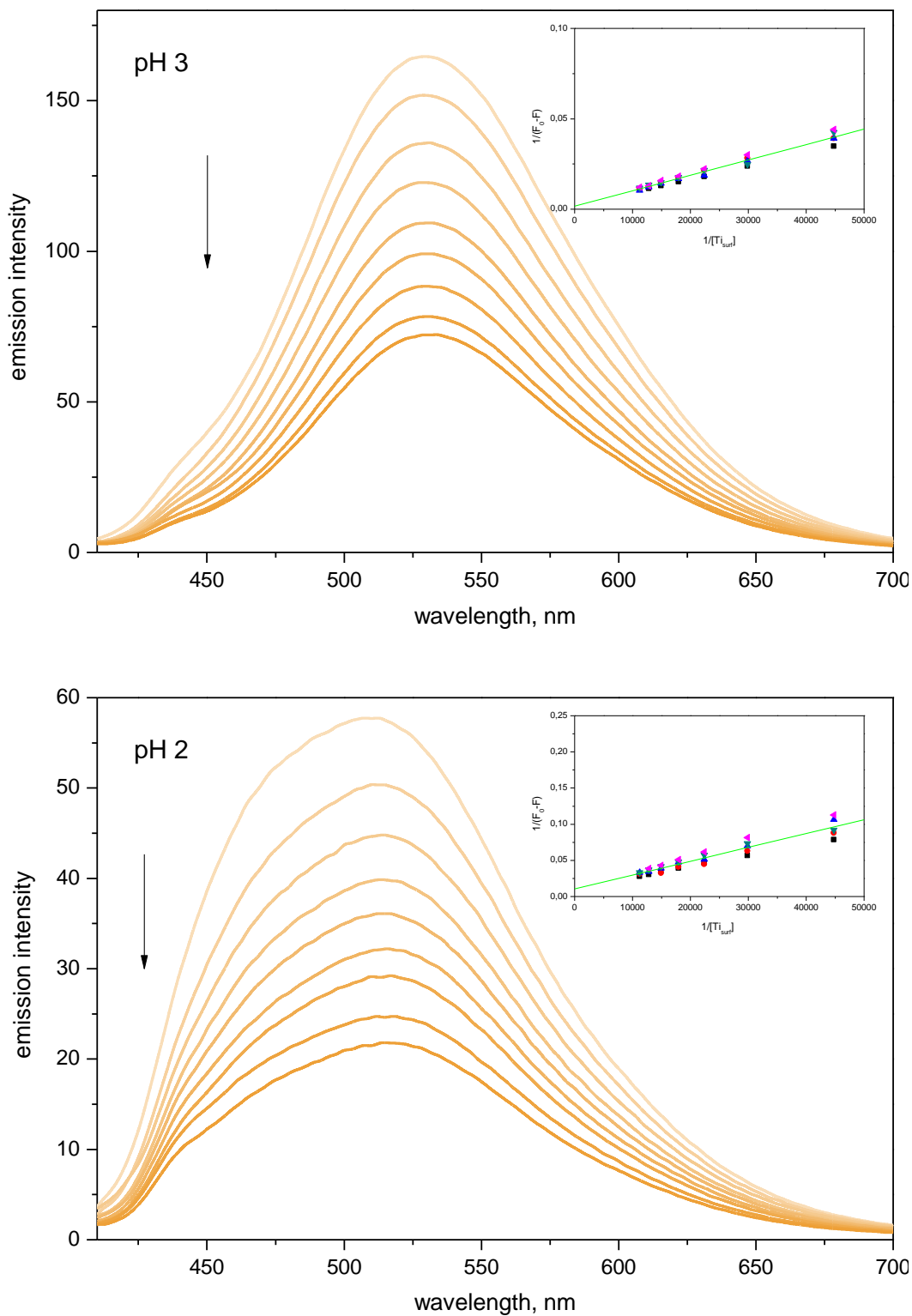


Figure S19. Emission spectra of 3,7DH2NA (50 μ M) in the presence of various concentrations of Ti_{surf} (0-90 μ M in 10 μ M steps) in aqueous solutions, at pH 2 and pH 3 (data recorded 20 h after surface modification). Inset: Benesi-Hildebrand plot for five series of measurements.

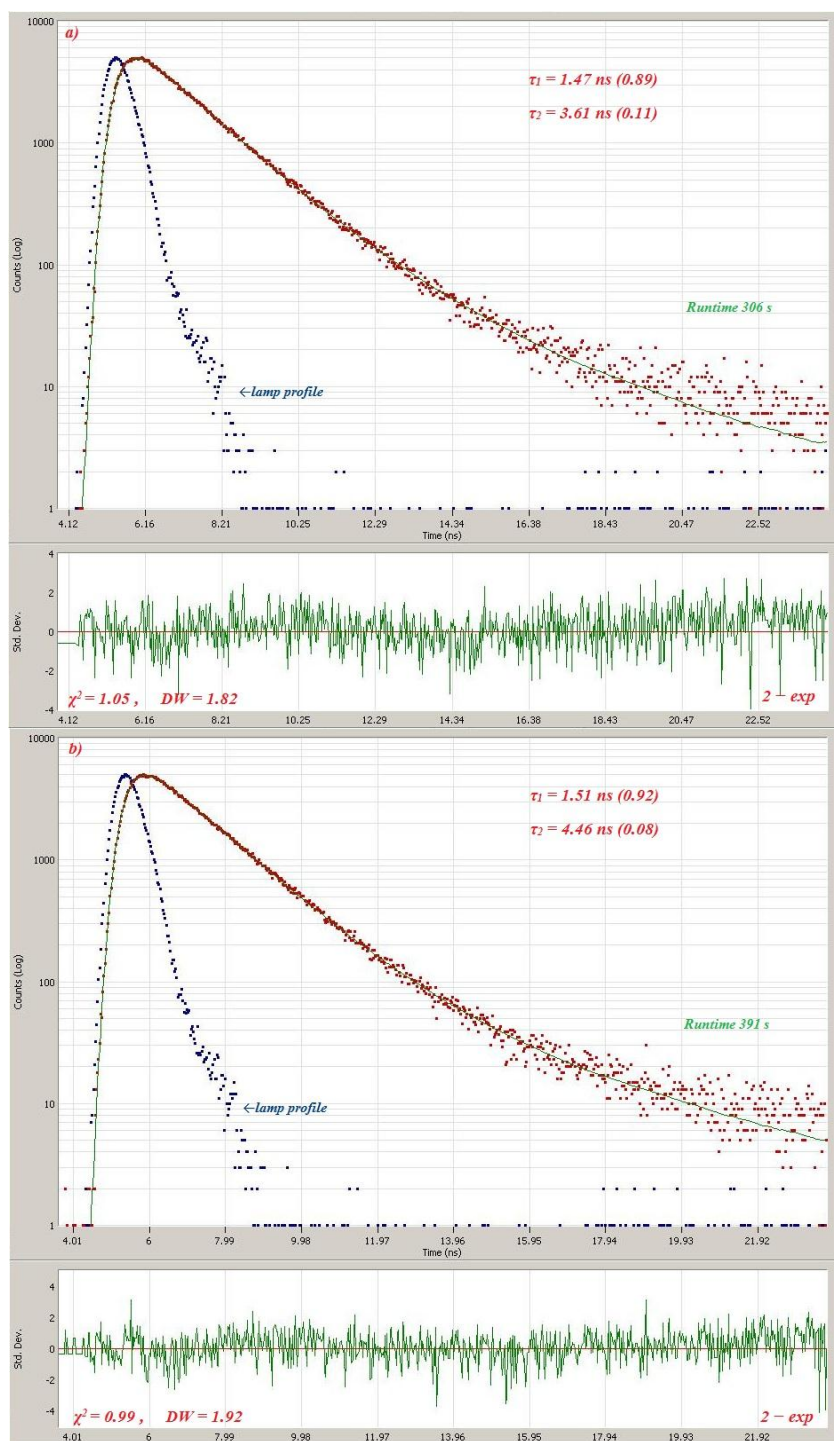


Figure S110. Time-resolved fluorescence decay profiles of 50 μM 3H2NA (a) and 50 μM 3H2NA + 20 μM Ti_{surf} (b) in aqueous solutions at pH 3. Excitation and emission wavelengths are 342 nm and 520 nm, respectively. The respective distribution of residuals, chi-square (χ^2) and Durbin-Watson (DW) parameters for biexponential fits are given below the fitted decay curves.

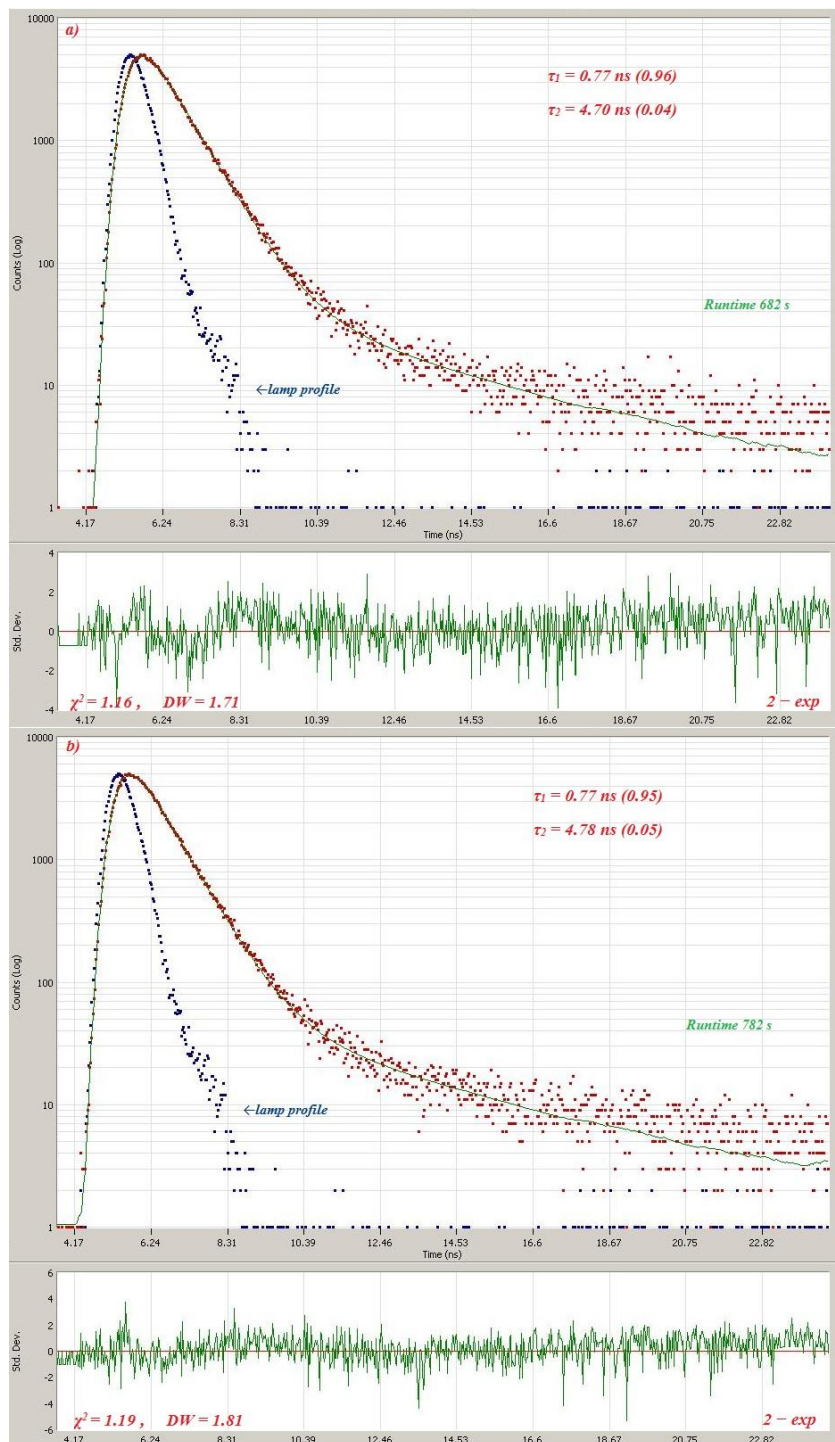


Figure S11. Time-resolved fluorescence decay profiles of 50 μM 3,5DH2NA (a) and 50 μM 3,5DH2NA + 20 μM Ti_{surf} (b) in aqueous solutions at pH 3. Excitation and emission wavelengths are 342 nm and 530 nm, respectively. The respective distribution of residuals, chi-square (χ^2) and Durbin-Watson (DW) parameters for biexponential fits are given below the fitted decay curves.

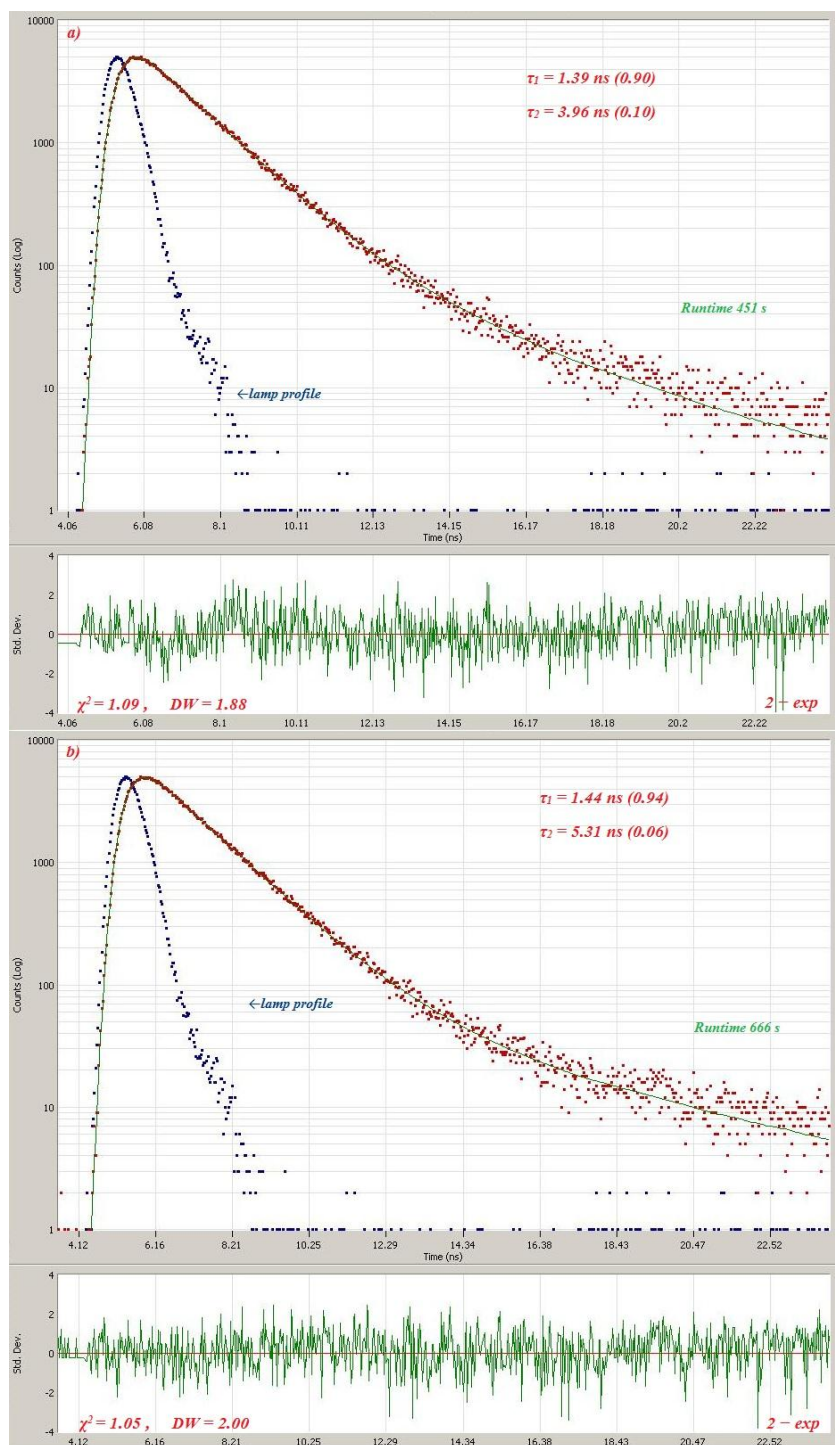


Figure S112. Time-resolved fluorescence decay profiles of 50 μM 3,7DH2NA (a) and 50 μM 3,7DH2NA + 20 μM Ti_{surf} (b) in aqueous solutions at pH 3. Excitation and emission wavelengths are 342 nm and 530 nm, respectively. The respective distribution of residuals, chi-square (χ^2) and Durbin-Watson (DW) parameters for biexponential fits are given below the fitted decay curves.

The ATR-FTIR spectra of 3, 5-dihydroxy-2-naphthoic acid, free and adsorbed on TiO₂ nanoparticles (Figure 6 of the manuscript). Bearing in mind the similarity between 3,5DH2NA and 3H2NA or 2HBA, the main bands could be assigned to free (protonated) acid¹⁻⁶ (curve A). The spectral region below 1200 cm⁻¹ is dominated by CH bending vibrations $\delta(\text{C-H})$ at 1015, 1065, 1111, 1157 and 1171 cm⁻¹. The bands in the region 1200 – 1400 cm⁻¹, namely at 1228, 1271, 1315, 1365, 1386 and 1398 cm⁻¹, could be assigned to the bending and/or stretching vibrations of the phenolic OH group (C_φ-OH), which is also strongly coupled with the stretching vibrations of the carboxylic group. The stretching vibrations of the benzene ring $\nu(\text{C=C})$ correspond to the bands above 1400 cm⁻¹, at 1441, 1459, 1519, 1574 and 1632 cm⁻¹. The pronounced vibration at 1662 cm⁻¹ existing only in the protonated form of the acid can be ascribed to the stretching vibration of the carbonyl group $\nu(\text{C=O})$. The vibrations of the carboxylic group are known to be coupled to the vibrations in the upper 1500's cm⁻¹ and lower 1600's cm⁻¹, i. e. 1574 and 1632 cm⁻¹, as well as to the 1441 cm⁻¹ band⁷. Upon the adsorption of 3, 5-dihydroxy-2-naphthoic acid onto TiO₂ nanoparticles (curve B) the greatest difference between spectra is observed in the region 1200 – 1400 cm⁻¹ where the bending and/or stretching vibrations of the phenolic OH groups (C_φ-OH) exist, as well as in bands where carboxylic group vibrations contribute. Hence, it is obvious that both groups take part in the chelation of titanium atoms. The intensity of the band at 1228 cm⁻¹ decreases, while the four bands in the 1300 – 1400 cm⁻¹ region produce one prominent band at 1390 cm⁻¹. The bands corresponding to vibrations in the carboxylic group at 1441 and 1662 cm⁻¹ almost entirely disappear, proving the deprotonation of the COOH group as a consequence of its binding to Ti atoms with the formation of a delocalized carboxylate group^{5, 8}. The appearance of bands at 1390 and 1596 cm⁻¹ can be attributed to carboxylate symmetric and asymmetric stretching vibrations^{1, 2, 5}, respectively. Ring

frequencies above 1400 cm^{-1} , assigned to $\nu(\text{C}=\text{C})$ vibrations are also affected by the new environment, indicating that the formation of the inner-sphere complex changes the electron distribution and symmetry of the ring⁴.

Unfortunately, since the characteristic doublet for the carboxylate symmetric stretching vibrations was not unequivocally observed $\Delta\nu(\text{CO}_2^-) = \nu(\text{CO}_2^-)_{\text{asym}} - \nu(\text{CO}_2^-)_{\text{sym}}$ value for 3,5-dihydroxy-2-naphthoic acid bound to the TiO_2 surface, this could not be used as the indication of surface structure of the CT-complex formed. However, the formation of a bidentate binuclear (bridging) complex could be proved from the Job's curve (Figure 2 of the manuscript) where the molar ratio between Ti_{surf} atoms and 3,5DH2NA in the complex is 2:1. This result is to be expected bearing in mind that 3,5DH2NA is structurally related to salicylic acid.

The ATR-FTIR spectra of 3, 7-dihydroxy-2-naphthoic acid, free and adsorbed on TiO_2 nanoparticles (Figure 7 of the manuscript). Considering the similarity between 3,7DH2NA and 3H2NA or 2HBA, the main bands can be assigned to free (protonated) acid¹⁻⁶ (curve A). The spectral region below 1200 cm^{-1} is dominated by CH bending vibrations $\delta(\text{C-H})$ at 1068, 1132, 1146 and 1183 cm^{-1} . The bands in the region $1200 - 1400\text{ cm}^{-1}$, specifically at 1200, 1215, 1258, 1287, 1337, 1361 and 1397 cm^{-1} , can be assigned to the bending and/or stretching vibrations of the phenolic OH group ($\text{C}_\phi\text{-OH}$), which is also strongly coupled with the stretching vibrations of the carboxylic group. The stretching vibrations of the benzene ring $\nu(\text{C}=\text{C})$ correspond to the bands above 1400 cm^{-1} , at 1436, 1456, 1481, 1528, 1583, 1614 and 1642 cm^{-1} . The pronounced vibration at 1692 cm^{-1} existing only in the protonated form of acid, could be the result of the stretching vibration of the carbonyl group $\nu(\text{C}=\text{O})$. The vibrations of the carbonyl group are known to be coupled to the vibrations in range of the upper 1500's

cm^{-1} and lower 1600's cm^{-1} ⁵, i. e. 1583, 1614 and 1642 cm^{-1} . Upon the adsorption of 3,7-dihydroxy-2-naphthoic acid onto TiO_2 nanoparticles (curve B) the greatest difference between spectra was observed in the region 1200 – 1400 cm^{-1} where the bending and/or stretching vibrations of phenolic OH groups ($\text{C}_\phi\text{-OH}$) exist with the contribution of carboxylic group vibrations. The most pronounced band appears at 1268 cm^{-1} implying the phenolic stretching interacts strongly with the titania surface⁵. The adsorption of 3,7DH2NA onto TiO_2 nanoparticles also leads to the almost complete disappearance of the band at 1692 cm^{-1} also affecting the bands at 1583, 1614 and 1642 cm^{-1} . Hence, it is obvious that both groups take part in the chelation of titanium atoms. The appearance of bands at 1358/1394 and 1604 cm^{-1} that can be attributed to carboxylate symmetric and asymmetric stretching vibrations^{1, 2}, respectively, as well as the disappearance of stretching vibration of the carbonyl group $\nu(\text{C=O})$ at 1692 cm^{-1} prove the deprotonation of the COOH group as the consequence of its binding to Ti atoms with the formation of a delocalized carboxylate group^{5, 8}. Ring frequencies $\nu(\text{C=C})$ in the region 1400 – 1500 cm^{-1} are also affected by the new environment, indicating that the formation of the inner-sphere complex changes the electron distribution and symmetry of the ring⁴.

Comparing the value of $\Delta\nu(\text{CO}_2^-) = \nu(\text{CO}_2^-)_{\text{asym}} - \nu(\text{CO}_2^-)_{\text{sym}} = 210/246 \text{ cm}^{-1}$, which we obtained for the case of TiO_2 bound 3,7DH2NA, with the corresponding value of $\Delta\nu(\text{CO}_2^-) = 231/245 \text{ cm}^{-1}$ given for the predicted 3-hydroxy-2-naphthoic acid monoanion⁵, one may conclude that a bidentate binuclear (bridging) complex is formed. This conclusion is further proved by the result obtained from the Job's curve (Figure 2 of the manuscript) where the molar ratio between Ti_{surf} atoms and 3,7DH2NA in the complex is 2:1. This result is to be expected, remembering that 3,7DH2NA is structurally related to salicylic acid and 3H2NA.

- (1) S. Tunesi and M. A. Anderson, *Langmuir*, 1992, **8**, 487-495.
- (2) E. C. Yost, M. I. Tejedor-Tejedor and M. A. Anderson, *Environ. Sci. Technol.* 1990, **24**, 822-828.
- (3) B. Humbert, M. Alnot and R. Quilès, *Spectrochim. Acta A* 1998, **54**, 465-476.
- (4) B. Rusch, K. Hanna and B. Humbert, *Environ. Sci. Technol.* 2010, **44**, 2447-2453.
- (5) E. M. Cooper and D. Vasudevan, *J Colloid Interface Sci* 2009, **333**, 85-96.
- (6) G. Socrates, *Infrared and Raman Characteristic Group Frequencies* , 3 rd Ed., John Wiley & Sons Ltd., England, 2001.
- (7) J. H. S. Green, W. Kynaston and A. S. Lindsey, *Spectrochim Acta* 1961, **17**, 486-502.
- (8) M. V. Biber and W. Stumm, *Environ. Sci. Technol.* 1994, **28**, 763-768.