Critical Role of Protons for Emission Quenching of Indoline Dyes in Solution and on Semiconductor Surfaces

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ABSTRACT: By combining time-correlated single photon counting (TCSPC) measurements, density functional theory (DFT), and time-dependent DFT (TD-DFT) calculations, we herein investigate the role of protons, in solutions and on semiconductor surfaces, for the emission quenching of indoline dyes. We show that the rhodanine acceptor moieties, and in particular the carbonyl oxygens, undergo protonation, leading to nonradiative excited-state deactivation. The presence of the carboxylic acid anchoring group, close to the rhodanine moiety, further facilitates the emission quenching, by establishing stable H-bond complexes with carboxylic acid quenchers, with high association constants, in both ground and excited states. This complexation favors the proton transfer process, at a low quencher concentration, in two ways: bringing close to the rhodanine unit the quencher and assisting the proton release from the acid by a partial-concerted proton donation from the close-by carboxylic group to the deprotonated acid. Esteriﬁcation of the carboxylic group, indeed, inhibits the ground-state complex formation with carboxylic acids and thus the quenching at a low quencher concentration. However, the rhodanine moiety in the ester form can still be the source of emission quenching through dynamic quenching mechanism with higher concentrations of protic solvents or carboxylic acids. Investigating this quenching process on mesoporous ZrO2, for solar cell applications, also reveals the sensitivity of the adsorbed excited rhodanine dyes toward adsorbed protons on surfaces. This has been conﬁrmed by using an organic base to remove surface protons and utilizing cyanoo-acrylic dye as a reference dye. Our study highlights the impact of selecting such acceptor group in the structural design of organic dyes for solar cell applications and the overlooked role of protons to quench the excited state for such chemical structures.

INTRODUCTION

Plenty of synthesizing organic dyes utilized in dye-sensitized solar cells (DSSCs), are based on the donor−linker−acceptor (D−π−A) architecture.1−5 Generally, these photosensitizers utilized in DSSCs have carboxylic acid units (COOH) as anchoring groups for strong adsorption on semiconductor surfaces. During the adsorption process, deprotonation takes place and the carboxylate group (COO−) covalently binds to the mesoporous substrate, via two undercoordinated surface Ti atoms. The resulted free proton is expected to be transferred to an oxygen atom on the metal oxide surfaces, closely to the adsorbed photosensitizer.6−10 However, the effect of such a close distance between the adsorbed proton and sensitizer on the excited-state dynamics of adsorbed sensitizers has not been investigated so far. To study such an effect, we selected the indoline dyes as a case of study, as it has been shown that protons can dramatically quench the excited-state lifetime of these dyes in solution.11−13 Indoline dyes consist of an indoline donor moiety, and different acceptor units; the better-known ones are D102, D149, D205, and D131 (see Figure 1 for molecular structures). The rhodanine (in D149, D205, and D102), and cyanoo-acrylic groups (in D131) are considered important acceptor moieties.4,12 The indoline sensitizers have shown high efficiencies (ca. ∼9.5%) in comparison to Ru complexes, under the same working conditions.13−15 In our

Figure 1. Chemical structure of the investigated indoline dyes showing the donor moiety and different acceptor groups, along with their abbreviated names.

the D149 is the best-performing dye within its family (9%),14,15 and its excited-state properties have been studied before by several spectroscopic techniques.16−20 In our
previous work, we found that protons, coming either from protic solvents or from the neighboring dyes, can effectively quench the excited D149. In protic solvents, such as alcohols, indeed, the emission decays were fitted by monoexponential decays, independent of the concentration for D149. On the contrary, in aprotic solvents, concentration—emission lifetime dependence was observed. Thus, a dimer formation was suspected for D149 in aprotic solvents. Also, the interactions with solvents showed emission lifetimes, which were inversely proportional to the hydrogen-bond donor strength of the solvent, suggesting a direct involvement of hydrogen bonds in the excited-state dynamics.

In fact, there are discrepancies in the literature reporting the highest-performing dye among the indoline dyes under different conditions. Nevertheless, D149 has better optical properties, such as higher oscillator strength and a red-shifted emission spectrum with respect to D131 and D102 (see Figure 2). These discrepancies motivated us to think that different cell fabrication and operative conditions may induce different excited-state deactivation pathways, thus reducing the electron injection efficiency of D149. For example, a previous study has shown that the presence of organic base (4-tert-butylpyridine) enhanced the performance of a dye with carboxylic group, while reduced the performance of the indoline family, we try to understand the relation between the dyes’ molecular structure and their excited-state lifetime in solutions and on semiconductor surfaces with respect to the quenching effects possibly induced by dimerization, solvent properties, and presence of protons. We combine experiments and quantum chemical calculations to answer the following questions: (I) what is the structure of the formed dimer in solutions? (II) do we have an effect of protons on adsorbed dyes on semiconductor surfaces? (III) which part of the dye is susceptible to undergo the protonation responsible for the fluorescence quenching? For the first question, we hypothesize dimer formation via the carboxylic anchoring group. The second and third questions are directly relevant to the design of optimal solar cell dyes, where deactivation pathways should be minimized. We show that the dye moiety susceptible of being protonated and responsible for the emission quenching in solutions and on semiconductor surfaces is the rhodanine ring and, in particular, its carbonyl oxygen. This study shows, for the first time, the influence of surface-adsorbed proton on quenching the dye’s excited state, depending on the peculiar dye structure, highlighting the importance of taking into account this aspect in the designing of a new high-performing photosensitizer.

II METHODS

Chemicals. The indoline dyes were obtained as a kind gift from Masakazu Takata, Mitsubishi Paper Mills, and used as received. The ethyl ester form of D149 (D149Ester) was also a kind gift from Prof. S. Uchida (Japan). The solvents, acetonitrile, toluene, CHCl₃ (Sigma-Aldrich, spectrophotometric grade), and methanol (MeOH) (Sigma-Aldrich, Chromasolve) are used without further purification. 1,8-Diabicyclo[5.4.0]undec-7-ene (DABCU, puriss., ≥99%) and chloroacetic acid (CAA) (puriss., ≥99%) were purchased from Fluka. All of the carboxylic acids and solvents used are purchased from Aldrich, Fluka, and are spectroscopic grades.

Steady-State Spectroscopy. Absorption spectra were measured on a Varian Cary 5000; emission measurements were performed using a Horiba Jobin Yvon Fluorolog and automatically corrected for wavelength-dependent instrument sensitivity. Solution measurements were carried out at a right angle in a 1 cm cuvette.

Time-Correlated Single Photon Counting (TCSPC). TCSPC has been previously described in detail. Briefly, the excitation of the sample was done with a picosecond diode laser (Edinburgh Instruments, EPL405) at 404.6 nm (instrument response function (IRF) ≈ 77.1 ps pulses). SpectraSolve was used for the TCSPC data analysis, as described before.

ZrO₂ Film Preparation and Sensitization. The preparation method for ZrO₂ film has been illustrated before in detail. Films were sensitized in a solution of D149 (0.1 mM) in different solvents as shown later in the text and dried afterward in vacuum for 10 min.

Quantum Chemical Calculations. All of the density functional theory (DFT), and time-dependent DFT (TD-DFT) calculations have been performed using Gaussian09 (G09) package. We studied, for both the ground (S₀) and lowest-energy excited (S₁) states, the interaction of D149 and one chloroacetic acid (D149CAA) and the formation of D149-D149 dimers. For the investigated systems, we performed S₀ and S₁ geometry optimizations in acetonitrile using the conductor-like polarizable continuum model (C-PCM) the B3LYP exchange and correlation functional, and the 6-31G* basis set. The accuracy of the B3LYP functional in reproducing the optical and structural properties of indoline dyes was benchmarked against experiments in some previous works. To refine the binding energy results, basis set superposition error (BSSE) correction has been applied. Since it has been suggested that the basis set truncation error can also be reduced by increasing the basis set, we have further verified the accuracy of our binding energy values by performing single-point calculations on the optimized structures using the 6-311+G* basis. Even if the calculated binding energies might be underestimated by the B3LYP functional because of the poor description of dispersion

![Figure 2. Absorption (solid line) and emission (dotted line) spectra for the D131, D102, and D149 dyes in toluene (excitation was at 500 nm for the emission measurements). The wavelength is the correct scale for the emission intensity.](image-url)

Table 1. Properties of the different dyes used in this study. (Continued...)

![Image of Table 1](image-url)
interactions, as shown previously, the relative energies of different hydrogen-bonded and halogen-bonded complexes are correctly reproduced. We can thus be confident of the qualitative information provided by the B3LYP results and use these data to individuate the electronegative site more prone to be protonated. Then, the effect of the protonation of the rhodanine carbonyl oxygens, being the electronegative sites most liable to be protonated, on the excited-state lifetime has been investigated by performing ground- and excited-state (S1) optimizations for the protonated species in acetonitrile and a relaxed energy scan in both S0 and S1 minima for the proton transfer from the chloroacetic acid to D149.

**RESULTS AND DISCUSSION**

**Time-Resolved Emission of Indoline Dyes.** Figure 2 shows the absorption and emission data for the studied dyes of the indoline family, D131, D102, and D149. While the D149 spectral positions are red-shifted ($\lambda_{\text{max}}^{\text{Absorption}} = 530 \text{ nm}$, $\lambda_{\text{max}}^{\text{emission}} = 590 \text{ nm}$), the D131 and D102 dyes have hypsochromic shifts in absorption ($\lambda_{\text{max}}^{\text{D102}} = 500 \text{ nm}$, $\lambda_{\text{max}}^{\text{D131}} = 450 \text{ nm}$) and emission spectra ($\lambda_{\text{max}}^{\text{D102}} = 560 \text{ nm}$, $\lambda_{\text{max}}^{\text{D131}} = 535 \text{ nm}$). The spectral positions of absorption and emission for these dyes depend on the strength of the acceptor moieties in the following order: cyano-acrylic < one rhodanine < two rhodanines. The absorption and emission spectra of the D149 dye were reported previously in different environments. The spectral shape and position of D149, D149Ester (the ester form of D149), and D205 dyes are similar; see Figure S1 in the Supporting Information (SI).

The previous emission lifetime measurements of D149 using TCSPC in various solvents illustrated the dependence of the observed lifetime on both the solvent properties and the utilized concentration of the D149. To connect these observations with the chemical structures, the D102 and
D205 dyes of similar structures were examined again in few selected solvents. As shown in Figure 3 and summarized in Table 1, the measured emission lifetimes of concentrated solutions of D102 (∼5–10 μM) in different solvents via TCSPC have the following results: CCl₄ (∼240 ps), CHCl₃ (∼750 ps), acetonitrile (∼350 ps), MeOH (∼70 ps), and acetonitrile-DABCU (∼630 ps). These emission lifetimes are similar to the ones reported for D149, where dimers of D102 and D205 are expected to be formed in nonpolar and aprotic solvents via the carboxylic groups, leading to short lifetimes (∼250–350 ps). However, the monomer species of these dyes (D149, D102, and D205) are shielded in other solvents like MeOH (∼70 ps) and CHCl₃ (∼750 ps). Proton solvents are expected to interact locally with the O or S atoms at the acceptor (rhodanine) moiety by forming O–H or S–H bonds, which are reinforced in the excited state due to the intramolecular charge transfer (CT) process from the indoline (donor) to the rhodanine (acceptor) group. This rearrangement of the solute–solvent, and consequently solvent–solvent H-bonds network, has been recently suggested to be responsible for the nonradiative excited-state quenching via the so-called hydrogen-bond-induced nonradiative deactivation (HBIND). Since CHCl₃ can locally interact, as H-bond donor, with the electronegative sites of the molecules (rhodanine, indoline, and COOH) but does not possess a network of H-bonds, the dissipation of energy to the solvent is not effective as in the MeOH case. This is also clear upon switching to CCl₄, in which short emission lifetimes were measured, as the dimerization is possible (see Table 1). However, in both cases, i.e., for MeOH and CHCl₃, interaction with the COOH group hinders the dimerization process. Although the properties of D102 resemble the ones of D149 in acetonitrile (i.e., dimers vs monomers), the D102 decays faster in MeOH (∼70 ps) than the D149 does (∼100 ps). This faster decay in D102 can be attributed to the more localized charge density on the first rhodanine moiety, as shown previously by Le Bahers et al. Also, the D102 shows a longer emission lifetime in MeOD rather than MeOH due to the expected slower HBIND process (see Figure S2). For the D205, the measured emission lifetimes are similar to those of D149, but with slightly longer emission lifetimes in all of the used solvents, which is mainly attributed to the long n-octyl chain that may hinder the previously detected isomerization process. This concentration dependence was slightly monitored for the D205 dye in nonpolar solvents, such as toluene, using absorption spectra via slight enhancement of the S₁ band, narrowing of S₁ band, and small blue shifts; see Figure S3. These observable changes in the absorption spectra for D205 imply that the n-octyl chain could reduce the association constant of the D205 monomers to be detectable by the conventional absorption measurements.

Previously, we analyzed the fluorescence decay of D149 as a function of concentration with a different carboxylic acid quencher (chloroacetic acid, CAA). As the measured emission lifetimes are a typical measure of the fluorescence yield and they are directly related to the quenching process, we had chosen to integrate, over a reasonable region, the total fluorescence from the TCSPC measurements and take the integral as a measure of the emission yield (for the same number of counts in the maximum channel). The advantage herein is, on the one hand, that fitting of emission lifetimes to the decay at nanomolar concentrations may be flawed by the presence of tiny amounts of impurities with relatively long lifetimes, and, on the other hand, that the TCSPC measurement itself is inherently independent on laser stability by virtue of its counting technique principle. Figure 4 displays the self-quenching behavior of D149 in acetonitrile using TCSPC; the integrated emission is plotted against D149 concentration in the inset. Two models were used for the best fit of the obtained data. The first one is based on the dimer formation of D149 in one step from two interacting D149 monomers (eq 1), which does not give a good fit to the obtained data (Figure 4).

\[
I = \frac{I_0 + 2I_\infty k_{eq}[C_0]^2(2k_{eq}C_0 + 1)^{-1/2}}{(1 + 2k_{eq}[C_0]^2(2k_{eq}C_0 + 1)^{-1/2})}
\]

where \(I\) stands for the complex emission; \(I_0\) and \(I_\infty\) are the monomer emission intensity at very dilute solution and the dimer emission intensity at a concentrated solution, respectively; and \(C_0\) is the initial concentration. The failure of this model is due to assuming that the dimer would emit two photons from the two monomers in the dimer complex. The second model gives a good fit and is based on a ground-state complex between D149 and quencher “another D149” (eq 2). In this model, we assume that only one photon is emitted per dimer, so one photon is in one photon is out.

\[
I = \frac{I_0 + I_\infty k_{eq}[D149]}{1 + k_{eq}[D149]}
\]

The extracted formation constant for the D149-D149 complex is \(\sim 1.25 \times 10^6 \text{ M}^{-1}\). The two dimeric configurations are almost isoenergetic, and their calculated binding energy is about 43 kJ/mol after BSSE correction (see Figure S5, Tables S1, and S2). The integrated emission for D102, and the formation
constant extracted from the emission data for the D102–D102 complex is $\sim 0.9 \times 10^6$ M$^{-1}$s$^{-1}$; see Figure S4. A lower dimerization constant of $\sim 0.34 \times 10^6$ M$^{-1}$ was found for the D205–D205 complex. The significant difference between the dimerization constants of D205, versus D149 and D102, is mainly attributed due to the presence of the n-octyl chain, which matches again with the observable variations in the absorption spectra for D205 (see Figure S3).

To experimentally confirm the role of the COOH group in the dimer formation, the D149Ester was also studied and, as expected, no concentration dependence was observed, due to the esterification of the carboxylic acid group (see Figure 3). Nevertheless, the obtained emission lifetime from the TCSPC for D149Ester in acetonitrile is 390 ps, contrary to the expected 700 ps for the monomer of D149. $^{21,39}$ This difference is, however, mainly attributed to the presence of impurities of protons from the esterification process of D149 that can quench the excited state of D149Ester. $^{21,39}$ This assumption has been confirmed by adding an organic base (DABCU) to the D149Ester in acetonitrile, which showed a longer-lived excited state of D149Ester with an emission lifetime close to 750 ps, similar to the emission lifetime of the monomers of D149, thus confirming the role of tiny traces of hydrogen ions for quenching the D149Ester. The impact of quenching by protons is also clear for measuring D149Ester in MeOH, where the measured emission lifetime is ca. 70 ps.

**Emission from D149 and D149Ester in the Presence of Quenchers Using TCSPC.** As discussed so far, esterification increases excited-state lifetimes by impeding dimerization via the COOH group at a high dye concentration. Here, we show how the esterification of carboxylic group can also affect the quenching process of D149 in solution at a low dye concentration, where dye dimerization can be ruled out. In Figure 6A, the integrated fluorescence of the D149 in the monomer case (nanomolar concentration of D149 was used) is shown as a function of the concentration for different quenchers. As is apparent, the fluorescence intensity of the monomers is reduced by water concentrations above ca. 0.1 M, while for carboxylic acid additives, the reduction of emission intensity is substantial already several orders of magnitude lower: ca. $10^{-5}$ M for chloroacetic acid and $10^{-4}$ M for formic acid. For the latter acids, two inflection points are seen, the second one is in a similar concentration region as the one for water, which is assigned to the diffusion quenching process, dynamic quenching.

Interestingly, repeating the same experiments with the D149Ester (see Figure 6B), different behaviors from the monomers of D149 are found; very similar quenching curves for all quenchers tested with strong emission quenching were observed only at concentrations above ca. 0.1 M, independent of the nature of the quencher (e.g., alcohol or acid). As pointed out previously $^{21}$, the low-concentration range of carboxylic acid ($10^{-4}$–$10^{-3}$ M) requires the acid quencher to be complexed with D149 in the ground state, as the average diffusion distances between D149 and a quencher are too large during the excited-state lifetimes (hundreds of ps), i.e., diffusion-controlled emission quenching mechanism is not

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**Figure 5.** Ground-state optimized geometries of the two possible D149–D149 dimers.

**Figure 6.** (A) Total fluorescence intensity of D149 in MeCN as a function of quencher concentration shown in the legend; low concentration of D149 was used to confirm the presence of monomers instead of dimers. (B) Total emission of D149Ester as a function of quencher concentration shown in the legend.
possible. Upon using water as an emission quencher, both D149 monomers and D149Ester behave similarly, and the emission quenching occurs at concentrations above 0.1 M. We can, therefore, attribute two quenching processes for D149: (1) a specific interaction between D149 and carboxylic acids (ground-state complex) at low concentrations through carboxylic acid group, and (2) an additional diffusion quenching process by water and alcohols at high concentrations (>0.1 M).

For the emission quenching via dimerization at a low concentration of carboxylic acids, we found that previous values of experimentally determined dimerization constants for some carboxylic acids in several solvents are between 5 and 4650 M$^{-1}$ (propionic acid in nitrobenzene and cyclohexane, respectively). And in the more polar nitrobenzene, the dimerization constants are strongly reduced compared to nonpolar n-heptane and cyclohexane. In the strongly polar acetonitrile, even lower dimerization should, therefore, be expected. On the other hand, to explain the association between D149 molecules at nanomolar concentrations, dimerization constants need to be approximately 10$^6$ M$^{-1}$. These high equilibrium constants for D149 with different carboxylic acids are attributed to the presence of the rhodanine moiety and carboxylic acid that allow for forming carboxylic complexes in the ground state, as we shall discuss later. For protic quenchers like water, ground-state complexes through carboxylic is not expected, but water molecules and protic solvents can still quench the excited-state of D149 through diffusion process since the used concentration of water is around 0.6 M (see Figure 6). For the D149Ester, the carboxylic acid is missing, so ground-state complexes with carboxylic acids are absent. However, D149Ester is still sensitive to the diffused protons from protic solvents and acids, as shown in Figure 6B, due to the presence of the rhodanine moiety in D149Ester similar to the D149 at a high concentration of emission quenchers. The excited-state lifetimes of the D131 dye (with cyan-acrylic acceptor group) showed similar dynamic behavior in acetonitrile and in MeOH (ca. 300–320 ps), excluding the sensitivity of the cyan-acrylic group toward interaction with protons as rhodanine dyes do. Thus, we can infer that the excited-state quenching by protons involves the rhodanine moiety and that the COOH group, being close to the rhodanine, also plays a major role, establishing a strong ground-state complex with the carboxylic acid, which is thus kept close to the rhodanine rings.

**Emission on the Semiconductor Surfaces (ZrO$\textsubscript{2}$)—Impact on the Performance of Solar Cells.** According to theoretical calculations, there are different ways for dye adsorption on semiconductor surfaces, and depending on the binding modes, electron injection and recombination can be affected. For the COOH group, a bridged bidentate (BB) anchoring mode is considered the most stable adsorption mode in the theoretical calculations and matches the FT-IR measurements for different dyes.

In the BB mode, the two oxygens of the COOH group form a covalent bond with two undercoordinated Ti atoms of (101) TiO$\textsubscript{2}$ anatase surface upon proton transfer to one surface oxygen atom. Dyes bearing the rhodanine-COOH anchoring functionality adopt a particular adsorption configuration on the semiconductor surfaces, with the molecule bent with respect to the surface plane (about 40–45$^\circ$) and the rhodanine moiety being very close to the surface (about 5–3 Å). Previous, it has been shown that the electrolyte used in DSSCs for D149 gave a higher efficiency of 23% (6.51→8%) if an organic base was used in the electrolyte. Later on, all of the electrolytes used with D149 were always containing organic bases.

Comparing the particular configuration of the D149–TiO$\textsubscript{2}$ interface, the presence of protons on the semiconductor, and the efficiency improvement obtained by addition of organic bases in the electrolyte, an important question arises: can we also have excited-state quenching phenomena by the adsorbed protons when the dye is anchored on the TiO$\textsubscript{2}$ surface? To answer this question, different studies have shown the effect of used solvents in the soaking baths on the dyes’ efficiencies in DSSCs without obvious reasons. However, the dissolved dye in the soaking bath has two main phases: the liquid phase and the semiconductor phase. In acetonitrile, we know that D149 and D205 are in monomer and dimer forms (mainly dimers at high concentration), while in MeOH, there are monomers only. However, D149Ester has only the monomer form in both solvents (acetonitrile and MeOH). Thus, D149, D205, and D149Ester were adsorbed on a high-band-gap semiconductor (ZrO$\textsubscript{2}$) from different soaking baths that contain acetonitrile, MeOH, and acetonitrile-DABCU, separately. After immersing the semiconductors for 3 h and drying them under vacuum for 10 min, the TCSPC has been used to investigate these dyes on ZrO$\textsubscript{2}$ through their emission decays. All of the fitted data needed biexponential lifetimes, as shown

| dye          | soaking solvent | $\tau_1$ (ps) | $\tau_2$ (ps) | $\tau_{eg}$ (ps) |
|--------------|-----------------|--------------|--------------|-----------------|
| D149         | acetonitrile    | 460 ± 16 (80%) | 1300 ± 40 (20%) | 628             |
|              | MeOH            | 380 ± 15 (61%) | 1100 ± 25 (39%) | 660             |
|              | acetonitrile-DABCU$^b$ | 900 ± 10 (66%) | 2230 ± 23 (34%) | 1352            |
| D149Ester    | acetonitrile    | 870 ± 15 (76%) | 2330 ± 40 (24%) | 1220            |
|              | MeOH            | 660 ± 16 (78%) | 1900 ±18 (22%) | 932             |
| D205         | acetonitrile    | 350 ± 19 (57%) | 1370 ± 33 (43%) | 788             |
|              | MeOH            | 400 ± 9 (60%)  | 1050 ± 24 (40%) | 660             |
|              | acetonitrile-DABCU$^b$ | 900 ± 20 (72%) | 2700 ± 39 (28%) | 1405            |
|              | CHCl$\textsubscript{3}$ | 401 ± 14 (65%) | 1050 ± 18 (35%) | 628             |
| D131         | acetonitrile    | 755 ± 41 (73%) | 3050 ± 38 (27%) | 1375            |
|              | acetonitrile-DABCU$^b$ | 1025 ± 12 (83%) | 3550 ± 180 (17%) | 1455            |

$^a$Lifetimes and amplitudes are in picosecond and percent, respectively. $^b$DABCU concentration is 10 times the dye concentration. $^c$DABCU concentration is 100 times the dye concentration.
in Table 2. The weighted-average lifetime ($\tau_{avg}$) was calculated to facilitate the comparison between different samples. For the D149 in acetonitrile and MeOH (see Table 2), the average lifetimes are very similar in both cases (\sim0.6 ns), so the monomer–dimer equilibrium in acetonitrile is not affecting the observed kinetics on ZrO$_2$. The addition of DABCU organic base to the soaking path (acetonitrile) showed interesting results. Two components, ca. 0.9 and 2.2 ns, are used for the best fit, and the average lifetime has been roughly doubled to be ca. 1.3 ns, instead of 0.6 ns in neat acetonitrile. This highlights that protons play a role in quenching the dye’s excited state on the ZrO$_2$ surfaces. One may think that the effect of DABCU base is similar to the effect of co-adsorbent agents like CDCA, which reduces the amount of dye aggregation on surfaces and increases the observed lifetimes. Such an effect of CDCA with D149 has been detected previously, where the lifetime of adsorbed D149 increases with the concentration used of CDCA.$^{17}$ To remove such a controversy, a higher amount of DABCU base was added to the soaking bath, as shown in Table 2, and no clear change of average lifetime was detected. Therefore, we can safely assign the effect of the organic base herein to the adsorption modes that reduce charge recombination. $^{49}$ Although using the organic base as an additive has been previously shown to affect the energy levels of the conduction band of TiO$_2$ and the electron injection kinetics, $^{50,51}$ we mainly attribute the effect of the organic base herein to the removal of surface protons.

Quantum Chemical Analysis. D149–CAA Complexation. Theoretical calculations can provide more detailed information about the energetic and the structure of the D149–CAA hydrogen-bonding complex. If we assume, as stated in the previous section and from the data in Figure S, that the dye–CAA complex should already exist in the S0 (ground state) because of the short excited-state lifetime of D149, we can also infer that this complex should remain stable also in the S1 (excited state) to transfer the proton responsible of the deactivation process. Due to the charge transfer nature of the lowest-energy excited state in D149, moving the electronic density from the indoline donor (the N electron-rich atom) to the rhodanine anchoring group, we can expect a consequent change in the topology and strength of CAA–D149 H-bond interactions going from S0 to S1, similarly to what was found by some of us for Z907 in protic solvents.$^{52,53}$ Thus, we examined various D149–CAA complexes by fully optimizing the structure in both ground and lowest-energy excited states, and considering all of the possible electron-rich atoms in the molecule and two different D149 isomers, termed D149a and D149b, differing for the rotation of the COOH anchoring group, as shown in Figure S5. While D149a is slightly more stable in S0 (about 2 kJ/mol), D149b, where the H-bond is established between the COOH unit and a carbonyl oxygen of the rhodanine, becomes the lower-energy structure in S1 (about 6 kJ/mol), as shown by the relative energies in Table S2. Exploring a large number of guess adducts structures by testing all of the possible electron-rich atoms and CAA orientations, we ended up, however, with the eight optimized systems displayed in Figures S5 and S6, since after relaxation, some of them converged into the same minima. The calculated relative stabilities are listed in Table S1.
and plotted in Figure 7. For the D149 dye, most of the electronegative atoms (S and O) are located on the anchoring moiety (rhodanine and carboxylic acid units) except one indole nitrogen in the donor unit. As it could be expected on the basis of the S0 → S1 charge flow, while the N-CAA H-bond is likely broken passing from the ground (1.91 Å) to the excited state (4.65 Å), an overall shortening in the H-bond lengths for excited-state geometries is observed for all of the complexes involving binding sites on the anchoring moiety (Figures S6 and S7). This change in the strength of H-bonding interactions is obviously reflected in the relative stability of the various complexes, shown in Figure 7, which also provides us with interesting additional information. In S0, the complexation via the carboxylic group is by far (>30 kJ/mol) the most stable one; H-bonds with the carbonyl oxygens of the rhodanine are largely preferred with respect to bonding to sulfur atoms (rhodanine) as well as to the nitrogen on the indoline core. In the excited state, D149-CAA_COOH is still the energetically favored adduct but complexation through the oxygens of the rhodanine rings is now considerably stabilized (about 10−15 kJ/mol) due to the S0 → S1 charge transfer and, consequently, the binding to the indoline N donor is slightly destabilized. A similar trend can be observed for the complexes with the S atoms on the anchoring, although the S0 to S1 stabilization is much lower.

The calculated binding energies for all of the investigated complexes in the ground state are gathered in Table S2. Interestingly, BSSE-corrected binding energies and the one obtained with 6-311+G* basis set are in overall fair agreement for most of the systems and correct the overestimation obtained with the small basis. We, however, note the slightly positive binding energy obtained after BSSE correction for D149a-CAA_N, an indication that the N indoline atom is unlikely to be the site of AAC complexation as it was suggested before. The carboxylic dimer is by far the most stable structure, with a calculated binding energy in the range of 60−40 kJ/mol, depending on the level of theory employed (Table S2), which nicely compares with the experimental values for the gas-phase dimer of −63.8 kJ/mol for acetic acid.

Up to this point, by cross-checking the experimental and theoretical results, the following conclusions can be drawn:

- Dye–dye dimerization responsible for fluorescence quenching in nonprotic solvents takes place via the carboxylic group;
- Protic solvents and carboxylic acids effectively quench the excited state by protonation of the rhodanine moieties both in solution and on the semiconductor surface;
- COOH establishes stable H-bond interactions with carboxylic acids in both the ground and excited states, which favor proton transfer to the close-by rhodanine moiety at a low quencher concentration;
- Interaction of CAA with the rhodanine ring is reinforced in the excited state, and the carbonyl oxygens are the electronegative atoms more liable to bind the acid and to undergo proton transfer.

What is still unknown is the possible mechanism of this proton transfer from CAA to the rhodanine oxygen and the effect of this protonation on the excited-state dynamics. A rough estimate of the ground- and excited-state energetics upon protonation of the rhodanine oxygen has been obtained by TD-DFT calculations in the S0 (Franck-Condon) and S1 in acetonitrile on the protonated D149 system (see Figures S6 and S7). For the neutral D149 in the ground-state minimum, the first and second excited states are calculated at 2.22 eV (558 nm) and 2.91 eV (426 nm), respectively. Upon protonation of the oxygen of the first rhodanine ring, the vertical excitations decrease to 1.91 eV (649 nm) and 2.32 eV (534 nm) for S1 and S2, respectively. At S1 equilibrium geometry, however, the S0–S1 energy difference, corresponding to the emission wavelength, dramatically reduces to 1.36 eV (911 nm), being now in the infrared region. This result nicely explains the fluorescence quenching by the protons observed in solution and on the ZrO2 surface for D149 and related indoline-rhodanine dyes.

To elucidate, however, the mechanism of this proton quenching when a proton donor, like a carboxylic acid or a strong protic solvent, is present and bounded to the dye already in the ground state, we performed a relaxed energy scan in both S0 and S1 for the transfer of the proton in a CAA–D149 complex, where the acid interacts by H-bonds with both the rhodanine oxygen and the carboxylic group (see the optimized S0 and S1 structures in Figures S8 and S9). One can indeed hypothesize that the COOH plays a double role in favoring the proton transfer, bringing close to the rhodanine unit the quencher by a stable ground-state complex on one side, and by assisting the proton release from the acid by “partially” donating its proton on the other side in a concerted mechanism.

The results are plotted in Figure 8, where also the first and last geometries of the scan are shown in the inset. As it could be expected, in the excited state (starting geometries in Figure
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Notes
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8), the HCAAO-ORhodanine bond is sizably reinforced with a shortening of about 0.1 Å of the H-bond, while the COOH-OCOOA interaction remains mostly unaffected and, as hypothesized, the COOH group equally assists the acid deprotonation in both the S0 and S1 H transfer, with a shortening of about 0.21 Å of the COOH-OCOOA hydrogen bond along the scan. Interestingly, while a sizable barrier of about 12 kcal/mol is calculated to transfer the proton in the ground state, the process is barrierless (less than 1 kcal/mol) in the excited state, suggesting an efficient excited-state quenching by proton transfer.

■ CONCLUSIONS

To conclude, we have shown that rhodanine moieties in the indoline dyes are responsible for the dye’s emission quenching by external protons. This proton quenching can happen in solution and on mesoporous semiconductor surfaces. The source of protons herein can come from protic solvents, carboxylic acids, or even adsorbed protons on surfaces. We have detected this phenomenon for different dyes, but mainly for D149 and its ester form, D149Ester. For D149, the proton quenching can occur primarily via ground-state complex and dynamic quenching processes in solutions. The absence of proton within the carboxylic group in the D149Ester makes the quenching happening only via dynamic quenching. On ZrO2 semiconductors, we could prove that the rhodanine moiety is still sensitive to the adsorbed nearby protons resulted from the adsorption process. The presence of protons nearby to the adsorbed dyes connected to the rhodanine moieties decreases the excited-state emission lifetimes of these dyes. This phenomenon is not detectable for D149Ester and D131, where protons and rhodanine moieties are absent, respectively. Quantum chemical calculations showed that ground-state complexation essentially happens through carboxylic acid groups, and that in the excited state, the carbonyl oxygens of the rhodanine rings are also liable to strongly interact with proton donors and thus undergo protonation. Proton transfer from the acid to the rhodanine oxygen was shown to be capable of efficiently quenching the dye’s emission and taking place without any energetical barrier in the excited state. These findings help to understand the role of the bases used in DSSCs and the relation to the dyes’ structures. Also, this study helps improve the molecular design of the dyes to avoid unnecessary deactivation pathways, which can reduce the efficiency within DSSCs.

■ ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acs.jpcc.0c07099.

Normalized absorption emission measurements and theoretical calculations on D149 (PDF)

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