# Control of photoswitching kinetics with strong light-matter coupling in a cavity

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**ABSTRACT:** Most photochemistry occurs in the regime of weak light-matter coupling, in which a molecule absorbs a photon and then performs photochemistry from its excited state. In the strong coupling regime, enhanced light-matter interactions between an optical field and multiple molecules lead to collective hybrid light-matter states called polaritons. This strong coupling leads to fundamental changes in the nature of the excited states including multi-molecule delocalized excitations, modified potential energy surfaces, and dramatically altered energy levels relative to non-coupled molecules. The effect of strong light-matter coupling on covalent photochemistry has not been well explored. Photoswitches undergo reversible intramolecular photoreactions that can be readily monitored spectroscopically. In this work, we study the effect of strong-light matter coupling on the kinetics of photoswitching within optical cavities. Reproducing prior experiments, photoswitching of spiropyran/merocyanine photoswitches is decelerated in a cavity. Fulgide photoswitches, however, show the opposite effect, with strong coupling accelerating photoswitching. While modified merocyanine switching can be explained by changes in radiative decay rates or the amount of light in the cavity, modified fulgide switching kinetics suggest direct changes to excited-state reaction kinetics.

## INTRODUCTION

Traditional photochemistry involves the interaction between a single absorber and a single photon. A molecule or complex absorbs a photon and is promoted to an electronically excited state from which it can perform various energy conversion processes and ultimately react intra- or intermolecularly. This model fails in the strong coupling regime in which the rate of energy exchange between light and matter is faster than dissipation processes. This regime is accessible when a photon mode interacts coherently with an ensemble of molecules so that the molecular excitation and cavity photon eigenmodes are replaced by new hybrid states that have both photonic and molecular excitonic characteristics. The new eigenmodes of the system are called the upper (UP) and lower polariton (LP), which correspond to the two branches of eigenenergies, respectively (Figure 1a).<sup>1</sup> The energy difference between the upper and lower polariton at resonance, which is referred to as the vacuum Rabi splitting, is given by Eq 1:

$$\hbar\Omega_{\rm R} = 2\sqrt{N}\hbar g_s \tag{1}$$

where  $\hbar g_s$  is the single particle light-molecule coupling strength, and *N* is the number of molecules in the ensemble. In addition to the polaritonic states, *N*-1 "dark" states emerge.<sup>1</sup>

Strong coupling between light and molecular excitations has emerged as a strategy to influence chemical reactivity. One common way to achieve strong coupling is to embed chromophores into a cavity that is resonant with the chromophore's transition (**Figure 1a**).<sup>2</sup> Coupling of vibrational excitations to infrared cavities has led to dramatic changes in thermal reaction rates.<sup>3–5</sup> The influence of optical polaritons on photochemical processes has received comparatively less attention. Although some works show negligible changes in photophysics due to strong coupling,<sup>6,7</sup> other studies of optical cavities have demonstrated polaritonic effects on spin or energy conversion processes such as intersystem crossing, triplet-triplet annihilation, resonant energy transfer, delayed fluorescence, and photobleaching.<sup>8–23</sup>

Only three experimental studies have investigated polaritonic effects on covalent photochemical reactions.<sup>24–26</sup> Photoswitches represent ideal systems in which to study polaritonic effects on photochemistry, since the isomerization of photoswitches is unimolecular, reversible, and easily monitored by spectral changes. Moreover, if only one isomer is able to couple to the cavity mode, a photoswitch-cavity system can be reversibly moved in and out of the strong coupling regime thanks to the dependence of Rabi splitting on the number of coupling molecules (**Figure 1b**).<sup>27</sup> In their seminal 2012 study, Hutchison *et al.* reported that the kinetics of the isomerization of a spiropyran (SPI)/merocyanine (MC) photoswitch was modified by coupling of the MC isomer to an optical cavity mode (**Figure 1c**).<sup>24</sup> Strong coupling to the cavity decreased the overall rate of attainment of photostationary state (PSS) and led to a PSS within the cavity containing a higher proportion of MC than the corresponding PSS outside of the cavity. The authors attributed both of these effects to



**Figure 1. (a)** Energy level diagram of the light-matter coupling process between an optical cavity mode and resonant molecules. Collective strong coupling leads to the emergence of two polaritonic states, upper (UP) and lower polariton (LP), and uncoupled dark states. (b) Illustration of photoswitching in an optical cavity. One isomer is uncoupled, and the visible-light absorbing isomer is capable of strong coupling. Photoswitching could then plausibly occur from either polaritonic state or the dark states. (c) The molecular structures and photoisomerization reaction of spiropyran (SPI)/merocyanine (MC) and fulgide molecules.

the change in energy levels introduced by strong coupling: the lower energy of the lower polariton relative to the non-coupled excited molecule led it to relax back to the ground state through cavity leakage, which thereby decreased the photoisomerization efficiency and increased the PSS MC concentration. A more recent report by Börjesson and coworkers studied the effect of strong coupling on the photoisomerization of a norbornadiene-quadricylane photoswitch system.<sup>28</sup> The authors did not study photoisomerization kinetics, but instead measured the quantum yield of the coupled and non-coupled system. They found that the quantum yield of photoisomerization upon excitation of the lower polariton state is significantly lower than that of the bare molecular exciton or of the upper polariton. The authors explained this effect as arising from a competition between cavity leakage and energetically unfavorable conversion to dark states following lower polariton excitation. Unlike in Hutchison's study, Börjesson et al. observed no change to photoswitching behavior when exciting to higher energy states than the lower polariton. In summary, previous studies of polaritonic effects on photoswitching have observed a suppression of photoswitching under strong lightmatter coupling conditions.

We herein expand experimental investigations of polaritonic photochemistry to a fulgide photoswitch (**Figure 1c**). Unlike the previously reported photoswitches discussed above, fulgides are P-type, meaning they do not engage in any thermal isomerization. Moreover, they switch between their open and closed states via a  $6\pi$  electrocylization/reversion mechanism, similar to diarylethenes, which is distinct from the previously reported photoswitches.<sup>29</sup> We additionally recapitulate Hutchison's original SPI/MC results in order to confidently compare the two photoswitches. We find that the two molecules exhibit different polaritonic effects: while the MC-to-SPI photoisomerization efficiency is decreased due to enhanced radiative relaxation, the analogous closed-to-open isomerization of the fulgide is enhanced in the strong coupling regime. We explain this effect as arising from an increase in the rate of fulgide ring opening under strong-light matter coupling conditions.

# **RESULTS AND DISCUSSION**

To maximize the change in concentration before and after irradiation (i.e. high PSS) and thus access larger Rabi splitting, we synthesized an all-visible-switching indolyl fulgide that has two isomers, open and closed (see Supporting Information (SI) for synthetic details and molecular spectra).<sup>30</sup> The fulgide molecules were dispersed in a polymethyl methacrylate (PMMA) matrix and put inside a Fabry-Pérot cavity that consists of two parallel silver mirrors deposited by thermal evaporation (Figure 2a). The Ag mirrors were intentionally designed with an asymmetric configuration, with the top mirror thinner than the bottom one by 20 nm to facilitate reflectance measurements (see Figure S1 for a detailed discussion). Two additional polyvinyl alcohol (PVA) layers were spin-coated to encapsulate the PMMA matrix and isolate the molecules from direct metal deposition and to avoid a plasmonic effect of silver.<sup>2,31</sup> A portion of the sample was masked during the top silver deposition, creating a region without the top silver mirror to directly measure the molecules outside a cavity, referred to as the off-cavity region. The region with top silver is referred to as the on-cavity region and the cavity mode is tuned to be resonant with the closed isomer absorption around  $\lambda_{max} = 670$  nm by controlling the layer thicknesses.

The fulgide cavity exhibited fully switchable strong coupling. The reflectance spectrum shows a sharp cavity mode following switching to the non-coupled, open state of the fulgide via red light irradiation (**Figure 2b**). Irradiation with blue light switched the fulgide to the closed state whose absorption is near resonant to the cavity mode. The closed isomer does not absorb blue light, leading to its accumulation. With long enough irradiation time, sufficient open isomers are converted to the closed form, and the cavity reaches strong coupling, as evidenced by the emergence of upper and lower polariton peaks in the reflectance spectrum. Measurement of the reflectance spectrum in the off-cavity region revealed a non-split molecular absorbance and can also indicate the concentration of closed form (**Figure 2c**). The fulgide photoswitches bidirectionally; therefore

the coupling strength can be tuned reversibly between no coupling and strong coupling.



**Figure 2. (a)** Schematic of the cavity samples used in this work. The photoswitch molecules in a PMMA polymer matrix are encapsulated by PVA buffer layers and two parallel silver mirrors. On-cavity measurements are made where both mirrors are present, while off-cavity measurements are made where there is no top mirror. (b) Reflectance spectrum of the on-cavity region shows a sharp cavity mode when the photoswitch is in the uncoupled isomer (blue), but switching to the coupled isomer leads to splitting into two broad polaritonic peaks (red), indicative of strong coupling. (c) Reflectance spectrum of the off-cavity region shows a single broad, switchable feature from the photoswitch. (d) Angle-resolved reflectance (TE polarization) of the cavity system in the open form. The purple dashed line marks the molecular transition. The cross markers show the extracted Lorentzian peaks from the spectra, and the white dashed line is obtained by fitting the data to a bare cavity dispersion model. (e) Angle-resolved reflectance in the closed form. The purple dashed line marks the molecular transition marks the cavity dispersion extracted from (a). The blue and red cross markers (solid lines) represent the peak energy (fitted dispersion) of the upper and lower polaritons.

To further illustrate the status of the system in open and closed forms, we measured the angle-resolved reflectance (TE polarization) of the sample using a Fourier spectroscopy technique. When the fulgide molecules are in open form, the cavity energy diagram has a single branch (Figure 2d). The resonance energy increases with the incidence angle and fits well with a bare cavity model. In closed form, the dispersion splits into two branches, corresponding to the upper and lower polaritons in the strongly coupled system (Figure 2e). The energy of two branches were fitted to a coupled oscillator model with dissipation<sup>32</sup> to extract the coupling strength parameter  $g = 199 \pm 5$  meV and calculate the Rabi splitting to be  $\hbar \Omega_R =$ 304  $\pm$  14 meV. By comparing the result to the exciton decay rate  $(\gamma_{exc}=271\pm10~meV)$  and cavity decay rate  $(\gamma_{cav}=13~\pm$ 1 meV), we verify that the conditions for strong coupling, 2g > $|\gamma_{\rm exc} - \gamma_{\rm cav}|$  and  $\hbar \Omega_R > \gamma_{\rm exc} + \gamma_{\rm cav}$ , are satisfied.<sup>33,34</sup> We also plotted the angle-dependent linewidth of the upper and lower polaritons in Figure S12, which exhibits a similar trend to the Hopfield coefficient of UP/LP, further confirming that the observed branches are indeed polaritons.

After fabricating and establishing the photoswitchability of the fulgide-containing cavity, we next measured and analyze the photoswitching kinetics. We began in the strong coupling regime with a maximized population of closed isomer, and irradiated the system with UV light at 325 nm. The use of UV irradiation simplifies the experiment because 1) silver has a transparency window near 325 nm, and 2) both isomers have similar absorption coefficients at 325 nm, regardless of coupling strength (**Figure S6**). Taken together, these two features of 325 nm irradiation mean that the amount of photons absorbed by the system does not depend on the coupling strength or distribution of isomers during the photoswitching experiment. Note that the visible light-absorbing closed fulgide will be excited into high lying excited states,  $S_n$ , by the UV light before quickly relaxing to the first excited state,  $S_1$ , or a polaritonic state, as depicted in **Figure 1b**.

We measured the reflectance spectra as a function of UV irradiation time as the closed isomers converted to the open form and eventually reached the PSS (**Figure 3a-c**). We modeled the reflectance using the transfer matrix method with the polymer matrix including molecules treated as a layer in the cavity characterized by a Lorentz oscillator model of the refractive index. The strongly coupled isomer concentration, which is proportional to the oscillator strength in the model, was extracted by fitting the reflectance spectrum at each irradiation time to the model, allowing for kinetics analysis. For a reaction at the photostationary state<sup>35</sup> with rate constant *k*, the concentration of the species of interest be written in a linear form by defining a quantity q(t) as

$$q(t) \equiv \ln \frac{[C]_t - [C]_{\infty}}{[C]_0 - [C]_{\infty}} = -kt$$
(2)

In Eq 2,  $[C]_t$  is the concentration of the closed isomer at time *t* and  $[C]_{\infty}$  is the concentration at the photostationary state (see SI "Data analysis" for additional details). The photoisomerization kinetics from closed isomers to open isomers upon UV irradiation is analyzed and plotted in **Figure 3d** and **3e**. Although we targeted the silver transparency window, the intensity of UV was different in the on cavity and off cavity regions, and we corrected this difference by fabricating and measuring an off-resonance cavity sample with thicker PMMA and PVA layer thicknesses with a cavity mode at 830 nm, spectrally distinct from any molecule absorption. Both on- and off-cavity kinetics in the off-resonance cavity show a linear trend (see **Figure S12** for the raw data before correction), and are well aligned after the light intensity correction (**Figure 3d**), which is expected in the absence of strong coupling. In the on-resonance sample, while the off-cavity result is still linear, the on-cavity result is clearly non-

linear (**Figure 3e**). At the beginning of the experiment, in the strong coupling regime, the magnitude of the slope is greater, but then gradually levels off to be parallel to the off-cavity data as the coupling strength decreases. Comparison to the non-resonant cavity indicates that the different behavior in the resonant cavity can be attributed entirely to strong coupling. The increase in the magnitude of the slope at early times, when the concentration of closed form is high, indicates that strong coupling acts to increase the rate of the closed-to-open photoswitching reaction. That is, in the fulgide cavity, strong coupling increases the rate of the photoreaction that depletes the strongly coupled isomer.

Similar measurements had been conducted with SPI/MC by Hutchison *et al.* previously.<sup>24</sup> In the SPI/MC system, the cavity acts to increase the concentration of MC at the 325 nm PSS. Further, the SPI/MC system approaches the PSS more slowly once it enters the strong coupling regime. According to Hutchison, these changes originate from an enhancement of the MC radiative decay rate in the strong coupling regime, which manifests as an overall decrease in photoswitching kinetics. In order to validate our comparison between fulgide and SPI/MC cavity modification, we recapitulated Hutchison's observations and data analysis (**Figure S11**). In summary, strong coupling increases the rate at which the fulgide cavity approaches the PSS, while it decreases the rate that the SPI/MC cavity does so.



**Figure 3. (a)** Illustration of the photoswitching reaction upon UV irradiation, starting from a full population of closed isomers to a mixture of closed and open isomers. **(b)** Reflection spectra of the on-cavity region as a function of UV irradiation time. The spectra are shifted in y-axis for better visualization. UV irradiation gradually brings the system out of strong coupling, as evidenced by the disappearance of Rabi splitting in the reflectance spectrum. **(c)** Reflection spectra of the off-cavity region as a function of UV irradiation time. UV irradiation gradually decreases the strength of the closed

isomer reflectance feature. (d) Calibrated reaction rate plot of an off-resonance fulgide cavity. Both off-cavity and on-cavity data exhibit linear trends, indicating no obvious rate change. A scale factor is applied to the plot such that the two lines overlap. (e) Calibrated reaction rate plot of a resonant fulgide cavity. Same scale factor as in (d) is applied. Modeling the photoswitching kinetics reveals accelerated switching in the strong coupling regime.

Spectrally, the two reactions look quite similar, with only the redshifted photoswitch isomer able to couple to the cavity. Analogously to Hutchison,<sup>24</sup> we here lay down a kinetic model that assumes the species  $C^*$ ,  $E^*$ , and I are in their stationary states, and the rate of excitation of both species is equal. A small difference between the kinetic models for the isomerization of the fulgide and the merocyanine is introduced to account for the fact that there is an intermediate state along the reaction coordinate when going from the closed isomer to the open isomer of the fulgide, but the backwards reaction proceeds in an ultrafast fashion.<sup>36</sup> This kinetic model is shown in Figure 4. Note that this kinetic model does not explicitly include the processes from the  $S_n$  into I after off-resonant pumping of C. Instead, since it involves several complicated ultrafast processes, they are incorporated in the rate constant  $k_2$ . The kinetic equation for the concentration of the closed isomer [C] is given by Eq 3 (see SI for a detailed explanation of the kinetic model).

$$\frac{d[C]}{dt} = -k([C]_t - [C]_{\infty})$$
(3)  
$$k = k_{EX,C} \left(\frac{k_2}{k_1 + k_2}\right) \left(\frac{k_3}{k_3 + k'_3}\right) + k_{EX,E} \left(\frac{k'_2}{k'_1 + k'_2}\right).$$

This kinetic equation yields Eq 2 upon integration (see SI for details), which implies that the speed at which the system reaches the PSS (the slopes in Figure 3d-e) is given by k.

where



**Figure 4.** Kinetic model for photoswitching of the fulgide.  $k_{EX,C}$  and  $k_{EX,E}$  are the excitation rates of the close and open isomers.  $k_1$  and  $k'_1$  are the sum of radiative and non-radiative decay rates of the closed and open isomers.  $k_2$  and  $k'_2$  are the rates from the corresponding excitons into the intermediate state and the ground state of the closed isomer.  $k_3$  and  $k'_3$  are the rates from the intermediate state to each of the reactants in the ground state. The shape of the potential energy surface for this reaction is taken from ref.<sup>36</sup>

Inside of the fulgide cavity, the kinetics are not well described by a time-independent rate constant k due to variation of the Rabi

splitting as the reaction proceeds. This non-linearity suggests that changes in k are due to changes in elementary rate constants involving the closed isomer  $(k_{EX,C}, k_1, k_2, k_3)$ , which is the only species present in the cavity initially. These changes in rate constants are consistent with the fact that k converges to the off-cavity case at long times when polaritons vanish, and that PSS concentrations in and out of the cavity are identical.

Theoretical models suggest that major polariton-induced modifications of excited-state reactivity occur near the ground state geometry.<sup>37–39</sup> Therefore, here we assume that  $k_3$  remains unchanged and we explain the differences between the on- and off-cavity rates as changes in  $k_{EX,C}$ ,  $k_1$ , or  $k_2$ . According to **Figure 3e**, k increases inside of the fulgide cavity at short times, which can be explained either by an increase in the excitation rate of the closed isomer  $(k_{EX,C})$  or its reaction efficiency  $\left(\frac{k_2}{k_1+k_2}\right)$ . This increase is the opposite of what is observed in the SPI/MC experiments, where both we and Hutchison observe a decrease in k in a resonant cavity.<sup>24</sup> The decrease in k can arise from an increase in the radiative decay  $k_1$  due to cavity leakage of the lower polariton, but it has recently been argued to be better correlated with the amount of UV light that passes through the mirrors (decrease in  $k_{EX}$ ).<sup>40</sup> For the fulgide cavity, effects of the modified photon density in the cavity leading to a change in radiative decay rate can be ruled out because the fulgide is negligibly fluorescent (**Figure S10**); <sup>29</sup> hence  $k_1$  can be regarded as mostly due to non-radiative decay. Although the optical filtering effect described by Thomas et al could describe the apparent decrease in photoisomerization in the SPI/MC system, we have reasons to believe this effect is not relevant to the fulgide system (*vide infra*).

In previous theoretical works, it has been shown that decay into the dark states is equivalent to local vibrational dynamics of the excited molecules.<sup>39</sup> If the reaction is slow compared to orthogonal deleterious processes (such as vibrational relaxation), the reaction will proceed like outside of the cavity. On the other hand, if the early-time dynamics ensues along the reaction coordinate (typical for ultrafast reactions), reactivity could be effectively modified by strong lightmatter coupling. We believe this latter scenario could be true for the fulgide system, consistent with previous works showing that indolylfulgide photoswitching proceeds faster than nonradiative decay from  $S_n$  to  $S_1$  (decay to dark states), and its rate has been shown to drastically depend on the pumping frequency.<sup>41</sup>

Based on the above reasoning, we believe the most plausible cause for the change in reactivity of the fulgide is collective strong coupling (increase in  $k_2$ ). In recent work, we have shown how a cavity can accelerate or decelerate excited-state reactivity for collectively coupled ensembles, despite the presence of large inhomogeneous broadening.<sup>42</sup> This mechanism is not based on modifications on the potential energy surface along the reaction coordinate, but on the fact that the cavity enables incident light to promote the system into excited states whose reactivity varies compared to outside of the cavity, even for equal excitation frequencies. The prerequisites are ultrafast excited state reactivity and pumping frequency dependence of the reaction outside of the cavity, which are both fulfilled for the fulgide system. This optical effect distinct from the one Thomas *et al* ascribe to the SPI/MC system, <sup>40</sup> which is based purely in a change in the amount of light that passes through the mirrors and varies with cavity properties such as its thickness, and does not require strong coupling. Such an optical filtering effect cannot explain why the fulgide photoswitching rate is increased at short times but converges to the exact same rate as outside of the cavity when strong coupling disappears. Nonetheless, it is possible that changes in the rate of photoswitching are due to changes in the absorption rate of the reactant inside the cavity (increase in  $k_{EX,C}$ ), and additional experiments such as time-dependent absorption measurements are needed to confirm or rule out this possibility.

# CONCLUSION

We studied the effect of strong light-matter coupling on the kinetics of photoswitching in optical cavities. We recapitulated previously published results in a spiropyran/merocyanine (SPI/MC) system in which strong coupling acts to suppress the photoisomerization between SPI and MC. We reported the first observation of polaritonenhanced photochemistry in a photoswitch system, in which the rate of photoisomerzation between two fulgide isomers is increased in the strong coupling regime. While the reproduced SPI/MC results can be explained by modification of radiative decay rates within the cavity or by a reduction in the amount of light available to trigger the photoreaction, modified switching of the negligibly fluorescent fulgides can currently best be explained by direct changes to excitedstate reaction kinetics within the cavity. At present, no theoretical model can explain these changes. The simulation of cavity-modified ultrafast dynamics and chemical reactivity to explain our observations, as well as other experimental results in the literature, will be the aim of future work.

## ASSOCIATED CONTENT

## **Supporting Information**

Materials and methods, experimental procedures, <sup>1</sup>H and <sup>13</sup>C NMR spectra, UV-vis and photoluminescence spectra

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