The traditional ways to control photochemical reactions range from chemical modifications to tuning the surrounding environment. Strong coupling between a molecule and light, achievable in resonant plasmonic cavities, provides an alternative toolbox to manipulate photochemistry. Here, by means of accurate quantum chemistry simulations, we show that it is possible to enhance the photoisomerization yield for azobenzene in a realistic setup with a mechanism that involves full complexity of the atomistic dynamics of the system.
SUMMARY

The strong coupling between molecules and photons in resonant cavities offers a new toolbox to manipulate photochemical reactions. Although the quenching of photochemical reactions in the strong coupling regimen has been demonstrated before, their enhancement has proven to be more elusive. Here, by means of a state-of-the-art approach, we show how the trans $\rightarrow$ cis photoisomerization quantum yield of azobenzene embedded in a realistic environment can be higher in polaritonic conditions than in the cavity-free case. We characterize the mechanism leading to such enhancement and discuss the conditions to push the photostationary state toward the unfavored reaction product. Our results provide a signature that the control of photochemical reactions through strong coupling can be extended from selective quenching to improvement of the quantum yields.

INTRODUCTION

The interaction between light and matter at the nanoscale is at the basis of a manifold of experimental applications in plasmonics, single-molecule spectroscopies, nanoprinting, and nanocavity optics. When light is sufficiently confined in micrometric or nanometric systems in the presence of one or more quantum emitters, its exchange of energy with the emitters becomes coherent and the system enters the strong coupling regimen. Accordingly, the degrees of freedom of light and matter mix and the states of the system are described as hybrids between the two: the polaritons. The first experimental realizations to pioneer the idea of controlling the chemical reactions through strong coupling of molecules with light made use of metallic cavities. Later on, the achievement of strong coupling with plasmonic nanocavities at the single-molecule level at room temperature has been obtained with a nanoparticle on a mirror (NPoM) setup. Such a setup has been recently improved with DNA origami for higher reproducibility. The manifold of possibilities opened up by such experiments drove efforts to explore microcavity-based setups at low temperature, achieving longer lifetimes for the whole system. Theoretical modeling followed immediately to survey the plethora of new possibilities offered by strong light-molecule coupling. The high flexibility of the polaritonic properties has been assessed for both realized and potential applications, giving rise to a new branch of chemistry: the so-called polaritonic chemistry.

When a resonant mode is coupled to electronic transitions, the molecules exhibit enhanced spontaneous emission at both the collective and single-molecule levels. When the coupling is sufficiently strong, coherent energy exchange...
occurs between light and photoactive molecules, potentially translating into modified photochemical properties. The modifications to the potential energy surfaces (PESs) (through all the current work) driving different photophysical and photochemical behaviors are described by a basis of direct products of electronic and photonic states. Under this assumption, the states of the system are best described as hybrids between electronic and photonic. 

The possibility to shape the electronic states with quantum light inspired various groups to explore the role of strong light-molecule coupling in controlling photochemical processes. For collective effects, the focus has been on polariton formation in full quantum diatomic molecules and several model dye molecules in a realistic environment. At the single-molecule level, the non-adiabatic dynamics schemes developed allowed for the prediction of features arising on the PESs such as the creation of avoided crossings and light-induced conical intersections (Colns), such features modify the shape of PESs, translating into a potentially different photochemical reactivity. The possibility to enhance the yield of photochemical processes has been recently proven for energy transfer, singlet fission, and catalyzed reactions through vibrational strong coupling, obtained by exploiting remote catalysts. For strong coupling with resonant optical frequencies, enhancement has only been suggested by calculations on model PESs and neglecting the cavity losses and realistic non-radiative events.

As such events play a central role in the yields of photochemical reactions, the question remains if strong coupling can lead to a real enhancement of photochemical quantum yields in real molecules. Even more practically, the interest resides in the photostationary regimen and in determining whether the related concentration of products is enriched with respect to the standard reaction conditions. Here, by means of the state-of-the-art approach we devised, we show that it is possible to identify conditions that lead to improved quantum yields and product-enriched photostationary states. By investigating azobenzene trans→cis photoisomerization in strong coupling, we compare to the zero-coupling case and highlight the differences between the two processes. Such a comparison allows us to propose an interpretation of the mechanism leading to the increased quantum yield for the trans→cis π→π* photoisomerization.

The model system we simulate is depicted in Figure 1 and mimics the experimental setup used by Baumberg and co-workers for achieving strong coupling with a single methylene blue chromophore. The azobenzene molecules are hosted in a one-to-one arrangement by cucurbit-7-uril ring molecules, which are in turn adsorbed on a planar gold surface. In this arrangement, the azobenzene long axis is approximately perpendicular to the surface. This is relevant because the field polarization and the transition dipole for the S0–S1 and the S0–S2 transitions are all aligned in the same direction. The cavity is completed by gold nanoparticles sitting on top of the cucurbituril ring and is much larger than the latter, so we simulate them as a second planar surface. Explicit water molecules fill the space between the gold layers (see Note S1).

RESULTS
Polaritons in Azobenzene
Before investigating the photochemical properties of molecules under strong coupling, we show how the coupling conditions affect the energy landscape in the

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case of multiple electronic states. In this section, we aim only to provide an interpretative framework for the results of the next section, and hence the results presented in this section are computed without environment.

In Figure 2, we present two relevant cuts of the polaritonic PESs for the isolated azobenzene molecule, one along the CNNC dihedral and the other along the symmetric NNC bending (symNNC). In the former, all other degrees of freedom and also symNNC were optimized for the ground state. In the latter, the analogous constrained optimization was done for each symNNC value, except that CNNC was fixed at $165^\circ$, in order to show a clear cut of the polaritonic avoided crossing modifying the dynamics (notice that at the trans planar geometry the $S_0, S_1$ transition dipole moment vanishes). We shall exploit the PESs presented in this section to act as a qualitative and conceptual aid. By doing so, we introduce the framework to discuss the mechanism leading to the enhanced yield of the photoisomerization reaction under realistic environment.

Even in absence of environment, when a single molecule is strongly coupled with a cavity, polaritons drastically affect its PES. The photochemical properties are, in turn, deeply affected by the shape of the polaritonic PESs. Aiming to thoroughly describe the molecule in the strong coupling regimen, we build the polaritonic Hamiltonian in the framework of a semiempirical wavefunction method:

$$H_{total} = H_{mol} + H_{cav} + H_{int}$$

(Equation 1)

Here, $H_{mol}$ is the semiempirical electronic Hamiltonian, $H_{cav}$ is the quantized electromagnetic field Hamiltonian for an effective resonant mode set at optical
frequencies, and $\hat{H}_{\text{int}}^{\text{SC}}$ is the quantum interaction between light and molecule in a dipolar fashion:

$$\hat{H}_{\text{int}}^{\text{SC}} = E_{1\text{ph}} \sum_{n,m} |n\rangle \langle n'| \lambda \cdot \mu(R)_{n,m} (\hat{b}^{\dagger} + \hat{b}).$$  \hspace{1cm} \text{(Equation 2)}$$

$E_{1\text{ph}}$ represents the magnitude of the single-photon electric field of the confined light mode, $\mu_{n,m}$ is the transition dipole moment between the electronic states, $\lambda$ is the field polarization unit vector, and $\hat{b}^{\dagger}$ and $\hat{b}$ are the bosonic creation and annihilation operators. The nuclear motion is treated classically, using the surface-hopping approach\textsuperscript{45} (see Experimental Procedures). By relying on a semiempirical wavefunction method, we provide a detailed description of the electronic structure at low computational cost. Such electronic structure method exploits a solid parameterization\textsuperscript{49} of the semiempirical electronic Hamiltonian and has been previously validated against experimental data in a number of applications.\textsuperscript{50–53}

To gain more insight on the features of the polaritonic PESs, we refer to the basis of uncoupled products of light and matter wavefunctions, given by the diagonalization
of $\hat{H}_{\text{mol}} + \hat{H}_{\text{cav}}$, labeled as $|n,p\rangle$. Here, $n$ (e.g., $S_0, S_1$) is the electronic state index and $p$ is the photon occupation number, either 0 or 1 in the present work. We consider a cavity photon of frequency 2.8 eV. Therefore, states with $p = 2$ lay at least 5.6 eV higher in energy than the ground state, i.e., more than 1 eV above our excitation window, which reaches up to 4.5 eV. Because of such a high energy difference, they cannot be populated during the dynamics, and therefore they are disregarded in our simulations of the photoisomerization dynamics (see Note S2). To clearly distinguish the uncoupled states in strong coupling and the electronic states in the zero-coupling frameworks, we refer to the set of uncoupled states $\{ |n,p\rangle \}$ with the ket notation, e.g., $|S_0, 1\rangle$ or $|S_1, 0\rangle$, whereas the zero-coupling electronic states $\{|n\rangle\}$ are named by the state label only, e.g., $S_0$, $S_1$. The polaritonic eigenstates of $\hat{H}_{\text{tot}}$, labeled as $|R_k\rangle$, are expressed in the $|n,p\rangle$ basis:

$$|R_k\rangle = \sum_{n,p} D_{n,p}^k |n,p\rangle.$$  \hspace{1cm} (Equation 3)

The coefficients $D_{n,p}^k$ of the uncoupled states in the wavefunction provide a simple interpretation for the system under strong coupling. The states with $p = 0$ represent no free photon in the cavity, the states with $p = 1$ represent one free photon in the cavity, and so on. In turn, the time-dependent polaritonic wavefunction can be expressed in either the polaritonic or the uncoupled basis set:

$$\Psi(t) = \sum_k C_k(t) |R_k\rangle = \sum_k C_k(t) \sum_{n,p} D_{n,p}^k |n,p\rangle.$$  \hspace{1cm} (Equation 4)

By the inclusion of the light-molecule interaction, a polaritonic avoided crossing or Coln is originated where the uncoupled states would cross. In Figure 2, we show such crossings along two reactive coordinates: the torsion of the CNNC dihedral and the symmNRC. Here, the states labeled as $p > 1$ are included in the PESs’ calculations, yet they are not included in the dynamics presented in the next section.

The Rabi splitting between the polaritonic states is proportional to the transition dipole moment between the electronic states at the correspondent crossing geometry for the uncoupled states through Equation 2. The magnitude of such splitting represents the coherent energy exchange rate between light and molecule in a confined system. In Figure 2C, we focus on the polaritonic avoided crossings laying in the trans region (CNNC 165°). We anticipate that such crossings deeply impact the photoisomerization mechanism of azobenzene, leading to enhanced trans $\rightarrow$ cis photoisomerization quantum yield.

**Photochemistry on Polaritonic States: Tuning the Photostationary Equilibrium**

In photoreversible processes, the ratio between the quantum yields of the direct and backward process determines the product yield $Q$ at the photostationary state,\textsuperscript{54} as shown in Equation 5

$$Q = \frac{|c|_w}{|c|_w + |t|_w} = \frac{J_{t\rightarrow c}}{J_{c\rightarrow t} + J_{t\rightarrow c}} = \frac{\epsilon_t \Phi_{t\rightarrow c}}{\epsilon_c \Phi_{c\rightarrow t} + \epsilon_t \Phi_{t\rightarrow c}}$$  \hspace{1cm} (Equation 5)

where $t$ and $c$ refer to the trans and cis isomers, respectively, $J$ is the reaction rate, $\epsilon$ is the molar extinction coefficient integrated over the excitation wavelength window, and $\Phi$ is the quantum yield. The quantities $|c|_w$ and $|t|_w$ are the asymptotic concentrations of the cis and trans isomers, respectively, which in this framework correspond to the cis and trans populations at the end of the dynamics. The ratio between the molar extinction coefficients depends on the excitation wavelength, and we shall assume $\epsilon_t/\epsilon_c = 7.9$ as determined by their integral average over the present.
excitation interval from the experimental data of azobenzene in methanol. Such a ratio impacts the position of the photostationary state, allowing it to shift selectively toward the cis and trans isomer depending on the irradiation wavelength. Nevertheless, the tunability is limited by the quantum yields of the individual processes, according to Equation 5. Aiming to manipulate the photostationary state position in azobenzene photoisomerization, we focus on improving the quantum yield of the unfavored process, namely the trans→cis photoisomerization.

To perform the polaritonic photoisomerization simulations, we exploit an on-the-fly surface-hopping approach and take into account all the nuclear degrees of freedom of azobenzene. Within this framework, the nuclear wavepacket moving on the polaritonic PESs is mimicked by a swarm of independent classical nuclear trajectories (see Experimental Procedures).

To build the polaritonic states, we sought a field frequency to maximize the quantum yields for the π→π* trans→cis photoisomerization. We set the cavity resonant frequency to 2.80 eV, which allows modification of the crucial region of the first excited state at CNNC close to 180° (detailed in Figure 2C) and the surrounding geometries, i.e., the region of the PESs where the geometry of the molecule starts to partially twist but it is essentially trans. The coupling strength $E_{\text{ph}}$ is 0.002 au, corresponding to a splitting of ~100 meV with a transition dipole of ~1 a.u. for the present case, consistent with the observed 80–100 meV in the experiment by Baumberg and co-workers. We sample the ground state distribution at thermostated room temperature. For each sampled configuration, we mimic the excitation by near-UV light with a central wavelength of 313 nm (3.96 eV) and a full bandwidth of 1 eV. The excitation window is chosen to include the absorption spectral features corresponding to the first π→π* transitions of trans- and cis-azobenzene, though a narrower excitation bandwidth centered at the same frequency yields the same results (see Note S1 and Figure 3). Upon absorption, the trajectories are vertically excited from the ground state to the polaritonic states. The excitation procedure is described in the Experimental Procedures section.

The polaritonic non-adiabatic dynamics simulations results are reported in Figure 3 (see Videos S1 and S2 for the dynamics with strong and zero coupling along the reactive coordinates). The capability of strong coupling to affect photochemistry is strikingly evident in Figure 3A, where we compare the population of trans and cis isomers for the trans→cis photoisomerization process obtained by zero and strong coupling. Such populations are evaluated at each time step by counting the number of trajectories with a CNNC dihedral greater (trans) and smaller (cis) than 90°. The populations are then normalized to the total number of trajectories.

Remarkably, the cis formation is significantly more efficient for the strong coupling. This is one of the main results of the present work, as the enhancement of a realistic reaction via electronic strong coupling has not been reported so far. As a first step to analyze the mechanism driving such an increased yield of product, in Figure 3B, we plot the fraction of reactive trajectories reaching CNNC<90° for each starting state separately. Each of such individual processes in strong coupling (orange lines) is indeed more efficient than the corresponding one in zero coupling (purple lines). The strong coupling processes are on average slower than the zero-coupling case,
i.e., the torsion around the N=N double bond is delayed, together with the decay to the ground state (Figures 4A and 4B). Although paradoxically contrasting with the higher yields observed with respect to the zero-coupling case, the slower dynamics offers a first hint to explain the change in the mechanism brought about by the strong coupling regimen, as detailed later in this work (see Video S3 for an example of the dynamics along a reactive trajectory).

The factor capable of both slowing the kinetics and increasing the quantum yields in polaritonic processes is the existence of the $jS_0^1$ state and its coupling with $jS_1^n$. Aiming to characterize the nature of the polaritonic states involved in the dynamics and to obtain a more meaningful comparison with the zero-coupling case, it is convenient to investigate the processes on the uncoupled state basis. To this aim, Figure 4A compares the uncoupled states’ populations (full lines) with those of the corresponding states in the zero coupling simulation (dashed lines, circle markers). Here, the population of the $jS_2^n$, $jS_3^n$, and $jS_4^n$ manifold is represented as $P_{\text{sum}}$ to highlight the relevant processes. The first striking difference is that the $S_1$ state in the zero-coupling case is populated quicker than in the strong-coupling case. In addition, a longer permanence of the trajectories on the $jS_1^n$ state is observed in strong coupling, mainly because part of the population oscillates between $jS_1^n$ and $jS_0^2$ (see Table S1). Consequently, $S_1$ (strong coupling) can be found still populated at times where $S_1$ (zero coupling) is already decayed (see Figure 4A). The role of the $jS_0^1$ state in delaying the depletion of $jS_0^1$ is to act as a supplementary reservoir for the $jS_1^1$ population during the first 400 fs. In fact, non-radiative electronic state decays from $jS_0^1$ are blocked given that the molecule is in its ground state.
The shape of the $\mathbf{R}_1$ and $\mathbf{R}_2$ PESs (see Figure 2) in the transoid region explains why the torsion is initially delayed in the strong-coupling case. Most of the hops that populate these two states go from $\mathbf{R}_3$ to $\mathbf{R}_2$ (i.e., essentially $\mathbf{S}_2$; 0) to the torsional and the symNNC motions (see Figure 2A), i.e., to the decrease of the CNNC dihedral and to the increase of both NNC angles. By partially populating $\mathbf{R}_2$, the progress along the reaction coordinate CNNC and the symNNC vibrational excitation are both hindered.

The association of slower torsional motion and slower $\mathbf{S}_1$; 0 decay with higher $\Phi_{c \rightarrow cis}$ quantum yield, which characterizes the strong coupling with respect to the zero-coupling case, is not so intuitive. Still, this effect is reminiscent of the same joint trends observed in simulations of the trans $\rightarrow$ cis photoisomerization in solvents of increasing viscosity, in agreement with experimental quantum yields and fluorescence lifetimes for the field-free case. A similar hindrance of the motion along the reaction coordinate, caused by strong coupling, was highlighted by Galego et al. by full quantum simulations but unavoidably led to suppression of the photoisomerization because the one-dimensional model cannot account for the competition between radiationless electronic transitions and geometry relaxation. Using a different one-dimensional model, Herrera and Spano showed how strong coupling can instead increase the electron transfer rate in disordered molecular ensembles.58

The reason why a slower progress along the reaction coordinate leads to a higher quantum yield for the realistic model we are using here can be found in the shape of the $\mathbf{S}_1$, $\mathbf{S}_0$ crossing seam. Note that, after leaving the surroundings of the
Franck-Condon region by twisting the N=N bond and/or increasing the symNNC angles, \(|R_1\) becomes almost pure \(|S_1, 0\). In the new region, its energy gets closer to that of \(|R_0\): a crossing seam between the two PESs exists. Even more, the crossing seam is practically unaltered with respect to the zero-coupling case (see Note S4 of the present work and Figure 1 in Cusati et al.\(^{50}\)). The energy minimum of such a seam (optimized CoIn) is found at a twisted geometry (CNCC = 95°), the seam is also accessible and coincides with the global minimum in \(S_1\), therefore, it is accessible even in the absence of vibrational excitation. However, the crossing seam can also be approached at larger CNCC values by opening the symNNC bond angles, as indicated by our semiempirical PESs and confirmed by accurate \textit{ab initio} calculations.\(^{59,60}\) At planar transoid geometries the seam is slightly higher in energy than the Franck-Condon point and much higher than the \(S_1\) minimum, so a strong excitation of the symNNC mode is needed to reach it. Recent work based on time-resolved spectroscopy has demonstrated the importance of the symNNC vibration, especially in the case of the \(S_0 \rightarrow S_2\) excitation.\(^ {60}\)

In zero coupling, the symNNC bending mode is excited once the \(S_1\) state is populated by internal conversion from \(S_2\), explainable by comparing the equilibrium values of the NNC angles in \(S_1\) and in \(S_0 / S_2\) (132° versus 118° and 110° at planar geometries). This excitation results in the opening of the symNNC angle and, in turn, promotes the internal conversion of \(S_1\) to the ground state by making the seam accessible at transoid regions, resulting in a rather low \(\text{trans} \rightarrow \text{cis}\) photoisomerization quantum yield. On the contrary, in strong coupling, the hindering of the twisting and bending motions discussed above decreases the extent of symNNC excitation. In fact, with more time spent at transoid geometries, symNNC is also quenched by vibrational energy transfer to other internal modes and the medium. As such, the detrimental effect of the symNNC on the \(\text{trans} \rightarrow \text{cis}\) photoisomerization quantum yield is partially suppressed. The essential role played by (at least) one additional vibrational mode other than the reaction coordinate shows the limitations of one-dimensional models, which might capture some essential features of the dynamics\(^ {60}\) but fail to faithfully describe molecules of useful complexity. Such limitation becomes critical in strong coupling as the PESs and the wavepacket motion are altered by the coupling along all modes. The present case gives a clear example of the need to resort to multi-dimensional models: the trajectories are steered away from the highly excited symNNC bending (zero coupling) toward the less excited symNNC bending (strong coupling). The alternative pathway due to strong coupling along a secondary coordinate is mainly reflected in the motion along the main isomerization coordinate, resulting in a higher yield pathway not predictable through the one-dimensional models.

The behavior hereby described is well highlighted in Figure 5, where we compare the distribution of the geometrical coordinates at the moment of the \(S_1 - S_0\) (\(|R_1\) – \(|R_0\)) hoppings in zero coupling (strong coupling), depicted for the non-reactive and reactive trajectories in the upper and lower panels, respectively. Additional data, including the hopping times, are also provided in Table S1. The reactive trajectories are shown to hop at CNCC closer to 90°, whereas the non-reactive ones count many hops at large values of both CNCC and symNNC. Moreover, a significantly wider distribution of symNNC is observed for the zero-coupling case (purple), a signature that the symNNC is more excited in zero coupling than in strong coupling. Large symNNC (symNNC > 150°) in zero coupling is accompanied by many hops at CNCC > 130°, confirming that the excitation of the symmetric NNC vibration promotes the internal conversion at transoid geometries. The narrower interval of symNNC for the strong-coupling case, instead, causes the trajectories to
hop (on the average) at more twisted geometries, accompanied by a higher probability of successful photoconversion to the cis isomer.

Until now, we have shown that the coherent exchange of energy between light and matter impacts both the kinetics of the dynamics and the mechanism, resulting in a non-trivial trend in the quantum yields. To verify the consequence of this result on the photostationary ratio of cis and trans populations, the cis → trans photoreaction at the same excitation frequency must be simulated as well. We found that such a process in strong coupling shows the same yield with respect to the zero-coupling case, $\Phi_{c} = 58\%$ and $\Phi_{t} = 61\%$, respectively. This is consequent to the more favorable slope of the PESs in the cis side, which also makes the cis → trans photoisomerization quantum yield insensitive to environmental hindrances.\textsuperscript{50,51,52} Going from the cis to the trans isomer, such steep PESs make the effect of the $|S_{0}, 1\rangle$ state

Figure 5. Non-reactive and Reactive Photoisomerization Dynamics for Strong Coupling and Zero Field upon $S_{1} − S_{0}$ Hopping

Non-reactive (upper) and reactive (lower) distributions of the reactive coordinates (symNDC and CNNC), computed upon the $S_{1} − S_{0}$ hops for the zero-field case (purple) and $|R_{1}\rangle − |R_{0}\rangle$ for the strong-coupling case (orange). The distributions, in particular the non-reactive one, show that high excitation of symNDC causes hops at less twisted CNNC values, resulting in a lower photoisomerization yield in zero coupling with respect to strong coupling.
in the dynamics almost irrelevant, resulting in the cis → trans photoisomerization occurring on much shorter timescales (150 fs, see Note S4) than in the trans → cis photoisomerization. Therefore, the substantial rise of the yields in the trans → cis process is sufficient to push the photostationary state toward the cis isomer.

When the system is in its free-photon state $|n, 1\rangle$, a loss of the photon can occur (e.g., by leakage from the cavity or absorbed by the cavity walls). As a consequence, the coherent exchange between light and matter is disrupted and the molecule collapses from a mixture of $|n', 0\rangle$ and $|n, 1\rangle$ states to $|n, 0\rangle$ only (see Experimental Procedures).

To test how robust the results seen above are with respect to photonic losses in the resonant cavity, we simulate the trans → cis and cis → trans photoisomerization processes in the presence of a finite cavity lifetime $\tau_{cav}$ and compare the so-obtained quantum yields to the zero-coupling case (see Figure 6). The photostationary state yield of cis product exceeds the zero-coupling one for $\tau_{cav} \geq 50$ fs (Figure 6A). Remarkably, this time is much shorter than the typical photoisomerization timescale, whereas intuitively one would expect that cavity lifetimes comparable to the photoisomerization time are needed to observe enhanced reactions. The photoisomerization timescales are longer than the permanence time of the trajectories on $|S_0, 1\rangle$, which is the only $|n, 1\rangle$ state with a non-negligible population at any time. Although the decay to the ground state and photoisomerization take around 800 fs to be completed, the average permanence time in $|S_0, 1\rangle$ can be estimated to about 35 fs from its time-dependent population. We see then why a photonic loss timescale much shorter than the timescale of the whole photochemical process is compatible with the observation of strong coupling effects. Below $\tau_{cav} = 100$ fs, however, the trans → cis conversion yield is quite sensitive to cavity lifetime. On the other hand, the cis → trans process is less affected because of the more favorable slope of the PESs and faster photoisomerization dynamics (see Figure 2 and Note S4).
DISCUSSION

By building the polaritonic states of azobenzene, we have shown how the molecular complexity can be taken into account for a single molecule strongly coupled to a resonator. The inclusion of a detailed treatment for the molecule and its environment allowed us to investigate the shape of single-molecule polaritons when a manifold of excited states are involved in the strong coupling.

We have shown that strong coupling deeply affects the dynamical processes taking place on polaritonic PESs. In particular, we have found a remarkable increase in the quantum yield of the $\pi - \pi^*$ trans $\rightarrow$ cis photoisomerization due to subtle changes in the mechanism: the shape of the polaritonic PESs and the time spent in the one-photon states bring about a lower degree of excitation of the symNNC vibration, which is the main cause of early decay from the $S_1$ state in zero-coupling conditions. As a result, under strong coupling more molecules reach a torsion of the N=N bond closer to cis before relaxing to the ground state and thus photoisomerize with a higher probability. By taking into account the backward reaction (cis $\rightarrow$ trans), such an effect results in an increase of the photostationary concentration of the cis isomer.

Through the simulation of a realistic system, i.e., by including the effects of environment and cavity losses, we could estimate a minimum cavity lifetime of 50 fs to observe a shift of the photostationary equilibrium toward higher trans $\rightarrow$ cis photoconversions. Although currently the lifetimes of typical plasmonic nanocavities do not exceed the 10 fs, new experiments are actively devising prototypical setups to achieve high reproducibility\textsuperscript{17,19,20} and longer lifetimes for these systems\textsuperscript{21,61} at the single-molecule level. The quickly growing interest in polaritonic applications bodes well for polaritonic devices to be exploited in real-life polaritonic chemistry.

Our results show promising possibilities in this field. Among them, the enhancement of the quantum yields and photostationary concentrations in experimentally achievable systems opens up a pathway toward a real control of photochemical reactions (i.e., quenching and enhancement). Concerning the role of polaritons in the photochemistry of single molecules, we think that the physics of polariton-mediated reactivity is far from being thoroughly investigated. Among the yet-to-be-explored possibilities, we mention multistate and bielectronic polaritonic processes, such as photoreactions mediated by excitation transfer.

EXPERIMENTAL PROCEDURES

Strong Coupling Hamiltonian

The Hamiltonian describing the system is given in Equation 1. Aiming to include all the degrees of freedom of azobenzene, we exploit a semiempirical Austin model 1 (AM1) Hamiltonian reparametrized for the first few electronic excited states of azobenzene.\textsuperscript{49} In addition, it includes the molecular interaction with the environment (see next section). The basis on which we build the polaritonic states is the set of electronic-adiabatic singlets $\{n\}$, from $S_0$ to $S_4$. The cavity Hamiltonian of the quantized electromagnetic field is:

$$\hat{H}_{\text{cav}} = \hbar \omega_{\text{cav}} \left( \hat{b}^\dagger \hat{b} + \frac{1}{2} \right)$$  \hspace{1cm} (Equation 6)

where $\omega_{\text{cav}}$ is the resonator frequency and $\hat{b}^\dagger$ and $\hat{b}$ are the bosonic creation and annihilation operators. As reported in the main text, the eigenvectors of the non-interacting Hamiltonian $\hat{H}_{\text{mol}} + \hat{H}_{\text{cav}}$ constitute the uncoupled state basis $\{n, \rho\}$. To obtain the polaritonic states (Equation 4) and energies, we selected a subset
of states \( |n,p\rangle \) of interest, in which we performed a confidence interval (CI) calculation including the dipolar light-molecule interaction at QM level (Equation 2), working in the coulomb gauge and long wavelength approximation. The stability of the dipolar approximation has been proven to break up when reaching high couplings\(^{62-65}\). To prove the robustness of such approximation in the current case, test calculations have been performed as in the previous work\(^{45}\) (see Note S3).

### Inclusion of the Environment

The environment is included at quantum mechanics/molecular mechanics (QM/MM) level interfaced with the electronic semiempirical Hamiltonian. The molecular Hamiltonian for the system is partitioned as\(^{66,67}\):

\[
\hat{H}_{\text{mol}} = \hat{H}_{\text{QM}} + \hat{H}_{\text{QM/MM}} + \hat{H}_{\text{MM}}.
\]  

(Equation 7)

The QM part is composed by the azobenzene molecule and the MM part is composed by the cucurbit-7-uril molecule (150 atoms), 710 water molecules, and eight frozen layers of gold encapsulating the system (418 atoms each, only van der Waals interactions). The force field used to evaluate the MM part is all-atom optimized potentials for liquid simulations (OPLS-AA) contained in the TINKER code.\(^{67}\) The QM/MM interactions are modeled by electrostatic embedding plus Lennard-Jones atom-atom potentials\(^{53,68,69}\) (see Note S1).

### Surface Hopping on Polaritonic States

After building the molecule embedded in the environment and optimizing the geometry at MM level, the equilibrium trajectory is run on the ground state by QM/MM dynamics. At the end of such dynamics, a few hundred of the initial conditions (nuclear phase space point and polaritonic or electronic state) are extracted by evaluating the transition probability from the ground state to the \( S_2, S_3, \) and \( S_4 \) electronic states (zero coupling) or \( |R_3\rangle, |R_4\rangle, |R_5\rangle \) polaritonic states (strong coupling). Both the zero coupling and strong coupling states are excited within the same energy window, i.e., centered at 3.96 eV (from 3.46 to 4.46 eV). More details can be found in Note S1.

The non-adiabatic molecular dynamics is performed by exploiting the direct trajectory surface-hopping approach.\(^{55}\) A few hundred classical nuclear trajectories (230 to 270) are computed on the fly on the polaritonic PESs independently. The hopping probability between the states is a modified version of Tully’s fewest switches.\(^{70}\) The modifications added take into account the strong coupling contributions\(^{45}\) and the decoherence corrections needed to properly describe the decoupling of wavepackets traveling on different states.\(^{56}\)

As usual in surface hopping, the population of a polaritonic state \( |R_m\rangle \) is represented by the fraction of trajectories evolving on \( |R_m\rangle \) (called the “current” state) at the given time. Consistently, the population of unmixed states \( |n,p\rangle \), shown in Figure 4A, are obtained by averaging \( |D_{n,p}^m|^2 \) over the full swarm of trajectories, where \( |R_m\rangle \) is again the current state.

### Cavity Losses

The decay probability to account for cavity losses is evaluated through a stochastic approach. In particular, it is taken to be proportional to the square of the coefficients of the uncoupled states \( |n,p\rangle \), with \( p>0 \) (\( p=1 \) in the present work), composing the time-dependent polaritonic wavefunction (see Equation 4):

\[
P_{\text{loss}} = \sum_{n,p\geq1} \frac{1}{\tau_{\text{cav}}} \left| \sum_m C_{nm} D_{n,p}^m \right|^2 = \sum_{n,p\geq1} P_{|n,p\rangle}.
\]  

(Equation 8)
Here, \( \tau_{\text{cav}} \) denotes the cavity lifetime while \( \Delta t \) is the integration time step. The decay probabilities referred to each state are indicated as \( P_{(n,1)} \), and \( n_{\text{st}} \) denotes the total number of electronic states included in the calculation. A uniform random number is generated between 0 and 1 and compared with the above interval. A check if the random number falls in any subinterval up to \( P_{(n,1)} \) is performed (see Figure 7). If that is the case, the photon is lost from \( |n,1\rangle \). The decay operator \( \hat{D}_{\text{off}} \) is then applied to the polaritonic wavefunction:

\[
\hat{D}_{\text{off}}|\Psi\rangle = |n',0\rangle|n',1\rangle|\Psi\rangle.
\] (Equation 9)

The arrival state \( |F\rangle \) is determined by taking the adiabatic state, which has the largest overlap \( \langle n', 0|F \rangle \) with the electronic state \( |n',0\rangle \). The dynamics is then resumed by taking \( |F\rangle \) as the new current state. We, hereby, point out that, for our current work, the decay always occurs from the \( |S_0,1\rangle \) state, as it is the only state with \( p > 0 \) with a non-negligible population during the dynamics. Even more, the arrival state is always \( |R_0\rangle \), as it is almost purely \( |S_0,0\rangle \) at all the relevant geometries (see Note S2). More generally, the wavefunction after the jump should be written as an electronic wave-packet, maintaining the possible electronic coherence present within the \( p > 0 \) manifold.

**DATA AND CODE AVAILABILITY**

The calculations were based on a locally modified version of MOPAC2002 and TINKER and are available from G.G. and M.P. upon reasonable request. The analysis and the Supplemental Videos are based on ad-hoc tools which are available from J.F. upon request.

**SUPPLEMENTAL INFORMATION**

Supplemental Information can be found online at https://doi.org/10.1016/j.chempr.2019.11.001.

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**AUTHOR CONTRIBUTIONS**

S.C. initiated this project; J.F., G.G., M.P., and S.C. designed the investigation; J.F. performed the calculations; all the authors contributed to the analysis of results and writing of the paper.
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