Photochemistry with Plane-Polarized Light: Controlling Photochemical Reactivity via Spatially Selective Excitation

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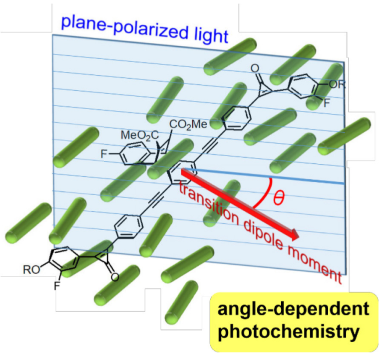
ABSTRACT: Photochemical reactions are intrinsically difficult to control because they involve high-energy excited state species. Herein, we report a novel approach towards controlling photochemical reactions via using spatially selective excitation of specific electronic transitions. This can be performed using photochemical irradiation with plane-polarized light of a photoreactive compound uniformly aligned in a nematic liquid crystalline (LC) medium. Having chosen cyclopropenone photodecarbonylation as a proof-of-concept reaction, we demonstrated that it could be controlled via changing an angle between the incident light polarization plane and the LC director. We showed that two specific partially forbidden electronic transitions were mostly responsible for this photochemical reaction. We envision that this simple general method can be useful in experimental studies of fundamental details of various photochemical processes, as well as can help to increase selectivity of photochemical transformations.

TOC GRAPHICS



KEYWORDS. Liquid crystals, photodecarbonylation, cyclopropenone, transition dipole moment, molecular alignment, polarization spectroscopy.

Photochemical reactions are intrinsically difficult to control due to the highly energetic excited state species involved in photochemistry. During the past five decades, remarkable progress has been achieved in the field of organic photochemistry in organized and constrained media developed as a principal way to control photochemical reactivity. Following the pioneering work by Schmidt on photochemical [2+2] dimerization of cinnamic acid derivatives in crystalline state,[1] many photochemical reactions of molecular crystals have been studied, and fundamental principles that control photochemistry in the crystalline solid state were uncovered.[2-4] Solid-state photochemical processes are often highly selective; a widely accepted (although somewhat qualitative) explanation of this selectivity, which is called the "topochemical principle", was introduced by Cohen in 1975 and described solid-state photochemical reactions as occurring inside a "reaction cavity", formed by neighboring molecules surrounding the reactant molecule. Since the reaction cavity in a molecular crystal provides a very rigid environment, the course of the reaction is dictated by the fit of the transition state geometry to the reaction cavity shape.[5] Thus, solid-state photochemistry is governed by strict geometrical constraints imposed on reactants by the three-dimensionally shaped rigid cavities.[6] A milestone development in this field was to replace the crystalline "reaction cavity" with less organized, softer media that would still provide some sort of a specifically shaped reaction cavity, although with less strict geometrical constraints. Such media include, although not limited to, inorganic porous or layered structures (clays and zeolites), organic polymers and dendrimers, self-assembled cavitands, micelles, liquid crystals, peptides, etc.[7-9] These materials provide a much "softer" reaction cavity and usually impose less restrictive "topochemical" demands. The main advantage here is that the choice of solid-state, crystalline rigid cavities is often limited to a small selection of possible crystalline polymorphs, whereas the more easily obtainable "soft" cavities provide a wider variety of convenient ways to manipulate and control photochemical reactivity.[10-15]

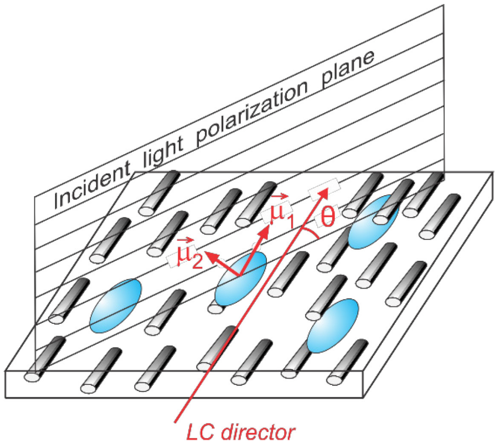
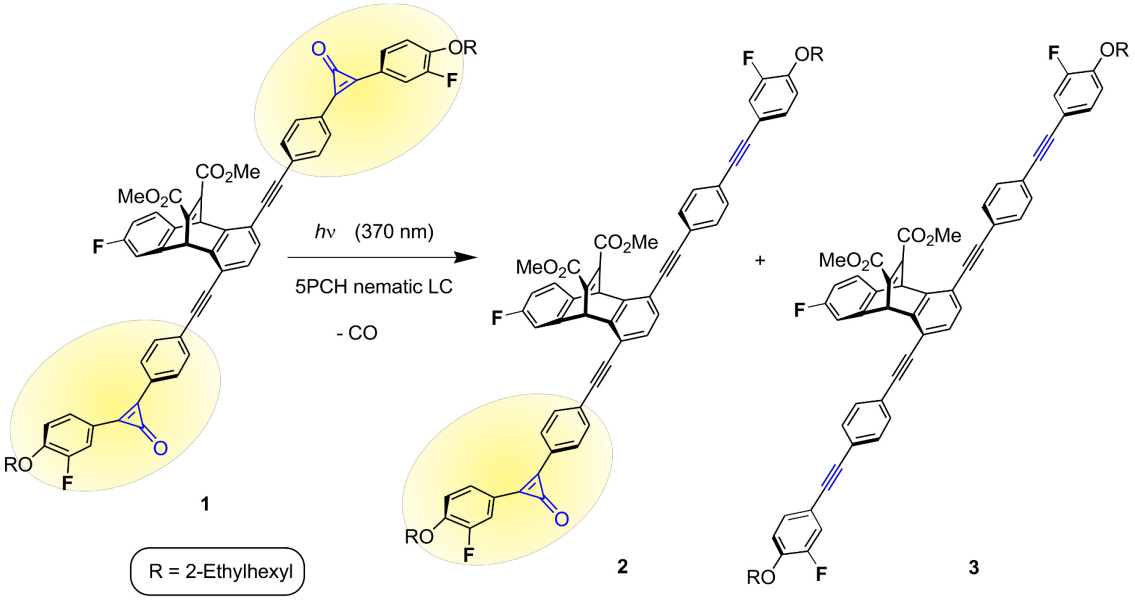


Figure 1. Schematic illustration of the interaction of incident plane-polarized light with an oriented guest – nematic LC host thin-layer sample. Cylinders represent nematic LC host molecules, and oval shapes are the dissolved aligned guest molecules.

From a mechanistic standpoint, a photochemical reaction starts with a vertical (Franck-Condon) excitation to an excited state, a process which is described by a corresponding transition dipole moment $\vec{\mu}$.[16] As a vector, it is characterized by magnitude and certain directionality. The directionality of $\vec{\mu}$ can potentially allow manipulating photochemical reactivity via selective excitation of a specific electronic transition, provided that the photoreactive compound is unidirectionally aligned in the bulk of the sample. Such alignment can be achieved in nematic liquid crystalline media. Liquid crystals (LCs) represent a unique class of liquids which, like crystalline solids, have some degree of long-range order. Specifically, nematic LCs are characterized by the one-dimensional long-range order. If a guest molecule is dissolved in the host nematic LC material, it will, on average, be oriented unidirectionally on a microscopic level, so the LC host framework provides mainly an orientational effect. The ability of LC host media to align and organize small guest molecules as well as macromolecules has been widely explored for materials applications, and is well documented.[17-26] Furthermore, as early as in 1970, Gray described using the orientational effect of a nematic LC solvent to carry out polarized IR spectroscopy on uniformly aligned metal-carbonyl complex guests.[27] Up to date, a relatively large body of work exists on general photochemical reactions in LC media.[28-32] However, in all these studies, the LC medium was employed as a source of a "soft" reaction cavity which provided some "topochemical" geometrical constraints for the reacting molecule, but could not significantly affect the photochemical reactivity.

Whereas the LC phase does not possess enough rigidity to efficiently control photochemical processes in a typical "topochemical principle" sense, it can be used to align and order the dissolved guest molecules before carrying out subsequent photochemical steps. Because of the nature of the nematic LC phase, the photoreactive guest molecules in the obtained system will possess a one-dimensional long-range translational order in the direction parallel to the LC director. An important consequence would be the possibility to <u>selectively excite different electronic transitions in the guest molecule</u> by irradiating the system with plane-polarized light. This is illustrated in Figure 1. The polarized light will preferentially excite the electronic transition that has a transition dipole moment $\vec{\mu}$ (or the projection of the transition dipole moment on the plane of the aligned sample) parallel to the electric field of the incident light. If the transition dipole moments corresponding to two different electronic transitions (e.g. transitions to S_1 and S_2 singlet excited states) are characterized by different spatial orientations, then it will be possible to selectively and independently excite each one of these transitions simply by changing the angle θ between the polarization plane of the incident light and the nematic LC director. Thus, this approach would enable exploiting spatial, rather than energetic, differences between the electronic transitions for controlling photochemical reactivity, without the need for geometric constraints of the "reaction cavity". Ideally, at some discrete values of the angle θ, a particular photoprocess would be "switched on", while at the other angles no photochemistry would occur. In addition to offering a simple (and surprisingly not yet explored) tool for controlling photochemical reactions without imposing rigid "reaction cavity", this approach would provide an experimental method to study photochemical mechanisms; specifically, it would enable direct experimental assessment of the transition dipoles and electronic excitations responsible for particular photochemical transformations, helping in correlating electronic transitions with experimentally observed photochemical reactivity.

Scheme 1. Photochemistry of compound **1** in nematic LC medium.



In order to test the proposed general concept, we chose to study photochemistry of compound **1** (Scheme 1). The two cyclopropenone units in **1** can undergo photodecarbonylation reaction furnishing either mono-decarbonylation product **2** or bis-decarbonylation product **3**.

Photodecarbonylation in cyclopropenones has been extensively studied by Popik,[33, 34] as well as by others.[35] This very efficient reaction with quantum yield approaching unity occurs in a singlet excited state, and has been developed into a foundation of an efficient photo-"click" strategy for biomedical and materials applications.[36-38] In compound **1**, the two cyclopropenone units are independent from each other, and therefore bis-decarbonylation product **3** should be furnished via two sequential decarbonylation acts with intermediate formation of the mono-decarbonylation product **2**. Therefore, in the conditions of incomplete conversion, the ratio of bis-decarbonylation product **3** to mono-decarbonylation product **2** serves as a reliable measure of the efficiency of photodecarbonylation in **1**. An important design feature was incorporation of a central barrelene (triptycene) unit to **1** in order to facilitate alignment of this rigid rod-like molecule in the nematic LC media (a consequence of the minimization of the large "internal free volume" effect[39, 40]). It should be noted that, although the central barrelene unit can also undergo photochemical di-π-methane rearrangement,[41] this reaction is not as efficient compared to the cyclopropenone decarbonylation, and would not happen to any noticeable extent within the timeframe of the decarbonylation reaction. Another key design feature included fluorine atoms attached both at the central barrelene and terminal cyclopropenone units. The fluorine atoms were added to act as NMR labels which could allow convenient analysis of the reaction mixture by ^{19}F NMR spectroscopy, without the need to separate photoproducts from the LC host.

First, we studied photochemistry of **1** in isotropic solution. Irradiation of a solution of **1** in THF using a handheld UV lamp (~365 nm) proceeded cleanly and efficiently, and resulted in quantitative formation of the bis-decarbonylation photoproduct **3**. In order to check more details on this photochemical reaction, we carried out irradiation of a THF solution of **1** using a low-power (100 μW cm^{-2}) monochromated light source at 370 nm. We specifically looked at the ratio of bis-decarbonylation product **3** to mono-decarbonylation product **2** at various conversions. At low conversion (4%), only mono-decarbonylation product **2** could be detected using ^{19}F NMR spectroscopy; however, as the conversion increased, bis-decarbonylation product **3** appeared, first as a minor product (ratio of **3** to **2** was 1 : 9 at 9% conversion), then gradually becoming the major product at higher conversions, and finally ending as the only product at 100% conversion (see Table S1 in the Supporting Information). Thus, we could conclude that the photoproduct **3** was indeed formed in two sequential photodecarbonylation steps, via intermediate formation of the photoproduct **2**, and therefore the ratio of **3** to **2** could indicate the efficiency of this photochemical reaction.

For detailed studies in LC media, we chose *trans*-4-(4-pentylcyclohexyl)benzonitrile (5PCH), which exists in nematic phase over a practically convenient temperature interval from 30 to 55 °C.[42] The problem of carrying out irradiation of a relatively large quantities of materials in macroscopically uniformly aligned LC media was not a trivial one. For this purpose, we fabricated special "preparatory" LC cells using 25 mm diameter quartz discs coated on one side with a 60-80 nm thick polyimide aligning surfaces which, prior to use, were rubbed in a single direction with velvet cloth to create aligning microgrooves. To make a cell, two of these discs were sandwiched together using a 20 μm thick Kapton ring gasket acting as a spacer. Each cell could hold ~6 μl of an LC solution of **1** – enough for an accurate ^{19}F NMR analysis, and could be rinsed with CH_2Cl_2 and reused multiple times. The details on the LC cells, as well as on the photochemical setup used in this study could be found in the Supporting Information. After filling with an LC solution of **1**, the cells were equilibrated 3 times by heating to 65 °C (a temperature above the LC's nematic-isotropic transition) and allowing to cool back to 40 °C, in order to maximize alignment of the photoreactive guest molecules along the LC director.

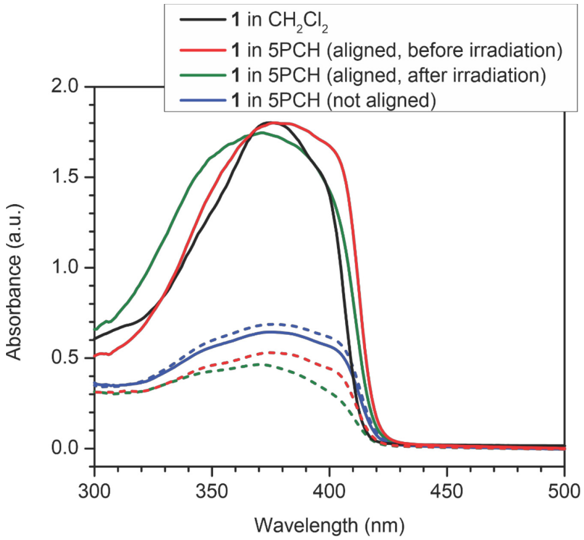


Figure 2. UV/vis absorption spectra of **1** in isotropic (CH_2Cl_2) solution and polarized absorption spectra of **1** in nematic LC (5PCH) solutions (conc. 0.25 wt. %) prior and after photochemical irradiation. For spectra in nematic LC solution, solid traces correspond to $A_{\|}$ and dashed traces correspond to $A_{\perp}$.

The UV/vis absorption spectrum of compound **1** in isotropic CH_2Cl_2 solution featured a band with a maximum at 372 nm and a long-wavelength shoulder at around 400 nm (Figure 2). This shoulder became significantly more prominent, and the long-wavelength offset of the absorption band shifted bathochromically for a solution of **1** in nematic LC phase. These changes indicated enhanced intramolecular π-electron conjugation upon dissolving **1** in the nematic LC phase.[43] We studied macroscopic alignment of **1** as 0.25 wt. % solution in 5PCH using UV/vis polarization spectroscopy (Figure 2). The 5PCH host showed no significant absorption above 300 nm (Figure S1 in the Supporting Information), therefore the absorption spectrum originated entirely from the photoreactive guest. The alignment of the guest is characterized by the order parameter S:

$$S = \frac{A_{\|} - A_{\perp}}{A_{\|} + 2A_{\perp}}$$

where $A_{\|}$ and $A_{\perp}$ are the absorbance values of the incident light polarized parallel and perpendicular with respect to the LC director.[26] The order parameter S can range between 1 (ideally aligned system) and 0 (isotropic system). For the guest **1**, the order parameter S (measured at 370 nm) was found to be 0.43±0.05, which corresponded to a moderately aligned system. To check if the alignment of the guest **1** was indeed caused by the aligning layers in the LC cell, we also checked polarized absorbance of the same solution in an LC cell without unidirectional aligning microgrooves on the polyimide coating surfaces (Figure 2). The order parameter S in that case was close to zero, indicating no preferential alignment. The optical absorbance of the nematic LC solution of the unidirectionally aligned guest **1** was about 3 times higher relative to the same but not aligned solution of **1**. This enhancement phenomenon is well recognized in polarization spectroscopy, and can be attributed to the high degree of the guest alignment.[44]

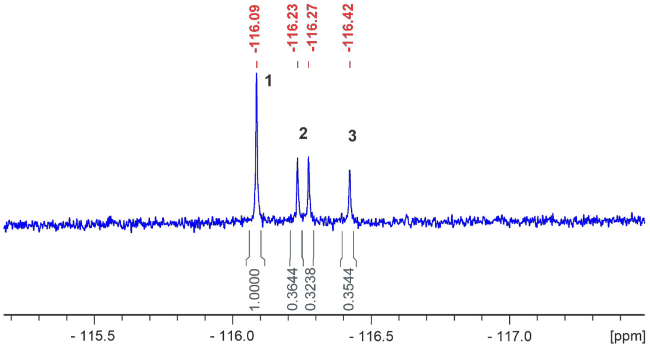


Figure 3. A representative ^{1}H-decoupled ^{19}F NMR spectrum (471 MHz, $CDCl_3$) of the reaction mixture after photoirradiation of **1** in 5PCH (region of barrelene F signals) showing assignment of the peaks.

To carry out photoirradiation with plane-polarized light of the aligned **1** in nematic LC phase, we built a photochemical setup consisting of a 300 W Xenon lamp equipped with a highthroughput monochromator set at 370 nm, and a 25 mm diameter wire-grid polarizer. The LC cell was mounted in a specially fabricated holder which could be rotated with respect to the polarization plane of the incident light; the temperature of the LC cell was kept at approx. 40 °C to maintain the nematic phase.

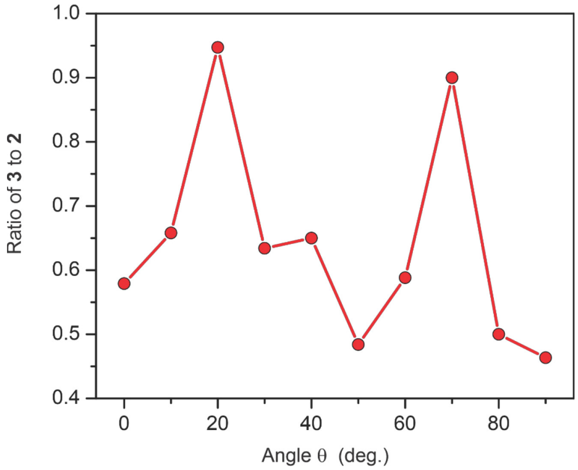


Figure 4. Ratio of photoproducts **3** to **2** as a function of angle *θ*.

Table 1. Photochemistry of **1** in Nematic LC Solution [a]

Angle *θ* (°) [b]	Total conv. (%) [c,d]	Product **2** (%) [d]	Product **3** (%) [d]	*S* before irradiation [e]	*S* after irradiation [e]
0	60	38	22	0.38	0.45
10	63	38	25	0.42	0.48
20	74	38	36	0.51	0.53
30	67	41	26	0.46	0.50
40	66	40	26	0.44	0.53
50	46	31	15	0.41	0.51

60	54	34	20	0.50	0.58
70	76	40	36	0.42	0.52
80	54	36	18	0.37	0.45
90	60	41	19	0.37	0.46

[a] Irradiation was carried out on 0.25 wt. % solutions of **1** in 5PCH in a specially designed LC cell (diameter 25 mm, thickness 20 μm) with unidirectionally grooved aligning surfaces, at wavelength 370 nm, with light power density 100 μW cm^{-2}, cell temperature approx. 40 °C, irradiation time 10 min. [b] The absolute error of angle measurement is 2°. [c] Sum of products **2** and **3**. [d] The product **2** and **3** amounts and total conversion were determined by ^{19}F NMR with a relative error of 10%; an average of at least two experimental runs is given. [e] Relative error of measurement is <0.5%.

In order to study the effect of the angle θ between the incident light polarization plane and the LC director on the photochemical outcome, we carried out the irradiation at 370 nm to incomplete conversions (in the conditions where both irradiation time and optical power density were kept the same, and the angle θ was changed from 0° to 90° in 10° increments). To confirm that the guest unidirectional alignment was not affected by the photochemical reaction, we checked the order parameter S after irradiation. We noticed an increase of this parameter (to 0.50±0.04) which was expected, considering that the straighter rod-like molecular geometry of both photoproducts **2** and **3** would further facilitate their alignment in nematic LC phase. The results of the photochemical runs are presented in Table 1. For the quantitative analysis of the reaction mixtures, we used high-resolution ^{19}F NMR spectroscopy carried out on the entire sample, without separating from the 5PCH host. The reaction mixture composition could be readily quantified using ^{19}F NMR signals of the fluorine atom attached to the barrelene unit (Figure 3). For nearly all values of θ, the conversion was within 45-65%, with mono-decarbonylation product **2** dominating. However, for the two values of θ, 20° and 70°, the conversion was noticeably higher, and the reaction yielded higher fraction of the bis-decarbonylation product **3**. This could be easily recognized on the graph showing ratio of the photoproducts **3** to **2**, which displayed characteristic spikes in the ratio at these two values of the θ angle (Figure 4).

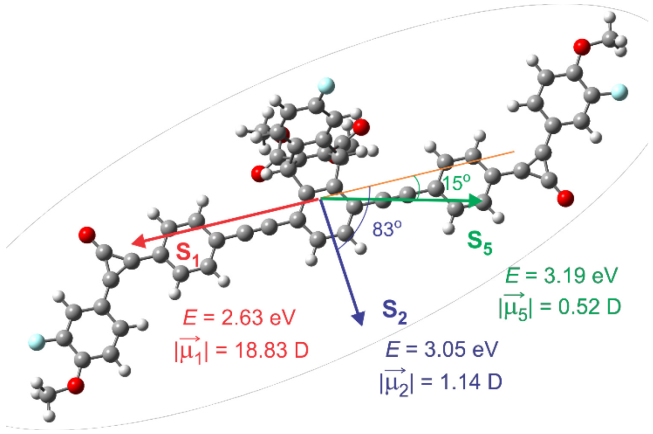


Figure 5. Optimized ground-state geometry of compound **1** (2-ethylhexyl substituents have been replaced with methyl groups to facilitate computations) and directions of the three transition dipole moments corresponding to vertical excitations to the states S_1, S_2, and S_5 (lengths of the vectors are arbitrary and don't reflect actual magnitudes). Also shown are the computed excitation energies and the magnitudes of the transition dipoles. Computations were carried out at B3LYP/6-31G* (ground state) and corresponding time-dependent method (excited states), using CPCM solvent treatment (acetonitrile).

Whereas we expected a strong angular dependence of the reaction outcome, we found it quite unusual that the photoreaction was more efficient at the two discrete positions different from a zero degree θ angle. Indeed, the dominant transition dipole moment in compound **1** corresponds to an electronically allowed π to π^* transition to the S_1 excited state in the elongated π system, and coincides with the long axis of the molecule of **1**. This transition shows the largest magnitude of the transition dipole moment (and hence the largest molar extinction coefficient), and therefore one would expect the more efficient photochemistry to happen when the incident light polarization plane coincides with the LC director (and thus the long axis of **1**). This, however, was not observed. Therefore, one could conclude that the electronically allowed transition to S_1 excited state was not the transition leading to decarbonylation in **1**. To help with understanding this outcome, we carried out time-dependent DFT computations on the first 6 vertical singlet excited states of **1**. We indeed found that the most intense transition corresponded to a π to π* excitation in the π-conjugated system of **1**, with a transition dipole moment coinciding with the long molecular axis (Figure 5). In addition, we found 5 other higher, but energetically close (lying between 3.05 and 3.26 eV) excited states with much smaller values of the transition dipole moments (indicating their partially forbidden nature). Natural Transition Orbitals (NTO) analysis[45] carried out on these excited states revealed that two of them, S_2 and S_5, were between the NTOs mainly located on the cyclopropenone units, and could be vaguely associated with π-π* and n-π* transitions on cyclopropenone (Figure 5 and S2 in the Supporting Information). Importantly, the transition dipole moments for these partially forbidden electronic transitions were significantly deviating from the long molecular axis (the calculated angles 83° and 15° with respect to the long molecular axis). These calculated directions were remarkably close to the values of angle θ of 70° and 20° which corresponded to the spikes in the products **3** to **2** ratio and thus indicated enhanced efficiency of the photodecarbonylation reaction. Some discrepancy between the calculated directions of the transition dipole moments and the experimentally observed values of the angle θ could be attributed to insufficient level of the DFT computations as well as difficulty with accurate modeling of the actual geometry of **1** in the unidirectionally aligned nematic LC medium. Nevertheless, the computational analysis could reasonably explain the experimentally observed results. Whereas photochemical reactions are often thought of as originating from the allowed electronic transition with the highest transition dipole moment (which predominantly leads to formation of the lowest excited state during conventional photoirradiation, due to the much higher molar extinction coefficient corresponding to its formation), we found instead that photodecarbonylation in **1** was primarily connected with the two partially forbidden electronic excitations with significantly smaller values of the transition dipole moments. In this case, using plane polarized light for the photoirradiation of a uniformly aligned photoreactive compound **1** enabled selective excitation of either of these two minor electronic transitions leading to enhanced photoreactivity.

In conclusion, we developed a simple experimental approach to perform spatially selective excitation of individual specific electronic transitions in photochemically reactive compounds. For the first time, we could experimentally correlate the outcome of a photochemical reaction (photodecarbonylation in cyclopropenone) with specific electronic transitions. We envision that this simple experimental technique will become useful in mechanistic studies of more complex organic photochemical transformations beyond the current proof-of-concept example, but also will provide a tool to carry out selective photochemical processes without geometric constraints of the "topochemical" reaction cavity.

ASSOCIATED CONTENT

Supporting Information. The supporting Information is available free of charge at https://pubs.acs.org. Detailed synthetic and experimental procedures, compounds characterization, and additional data and figures.

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Notes

The authors declare no competing financial interests.

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