Ultrafast Dynamics of Electronically Excited Host–Guest Complexes of Cucurbiturils with Styryl Dyes

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ABSTRACT: The relaxation mechanism of electronically excited states of host–guest complexes between cucurbiturils (CB) and pyridinium styryl dyes is considered in detail on the basis of the recent results obtained by the up-conversion fluorescence technique. The addition of CB to aqueous dye solutions increases the longest fluorescence decay times from about 50 ps for the free dyes to 100–150 ps for the bound ones. This is attributed to the braking of intramolecular rotations around the single bonds of the styryl moiety that is provided by guest’s displacement inside the cavity, whose driving force is a Coulombic interaction of the styryl dye cation and negatively charged CB portals. This displacement, a translational movement along the CB axis, is associated with the observed decay time of about 1 ps. There is also a characteristic time of about 100 fs, attributed to vibrational relaxation. In fact, such complexes can operate as a molecular machine, the molecular switch.

INTRODUCTION

Since the beginning of this century, there has been a significant increase in publications on physical chemistry of cucurbit[n]-urils (CB[n]), macrocyclic cavitands that consist of n glycoluril units (n = 5–8) bound by pairs of methylene groups. Depending on the number of glycoluril fragments, the inner equatorial diameter of the cavitands varies from 4.4 to 8.8 Å as the height of 9.1 Å is constant for all macrocycles (the chemical structure is shown in Figure 1).

Figure 1. Structures of CB[n] and styryl dyes.

This increase of research activity can be attributed, to a certain extent, to the ability of cucurbiturils, whose both portals carry a considerable negative charge, to form stable host–guest complexes with cations of appropriate size (for a recent review, see ref 2). What matters is that the production of complexes commonly results in a significant change in the physicochemical features of a guest molecule. In particular, the ability of the cucurbituril inclusion complexes of organic dyes to increase the fluorescence quantum yield of the guest molecule is of great significance for possible practical application in various fields of applied and fundamental science.

This can be best illustrated by a specific example: Li and co-workers3 have observed that the fluorescence of aqueous solution of a styryl dye, trans-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide (1) (the chemical structure of 1 is shown in Figure 1) increases 270 times upon addition of CB[6]. The binding constant of 1:1 complexes obtained by fluorescence titration was found to be $1 \times 10^5$ M$^{-1}$. Quantum–chemical calculations, which are confirmed by NMR measurements, have shown that in the case of the ground state of the host–guest complex, the positively charged pyridinium group of the dye is inserted in the cavity as its larger styryl moiety is placed outside the cavitand. Also, it turns out that such a structure of complexes is common at least for complexes with styryl dyes. The same structure of inclusion complexes with CB[7], whose binding constant is about $10^6$ M$^{-1}$, was found for a close analogue of 1, 4-[[(E)-2-(3,4-dimethoxyphenyl)ethenyl]-1-ethylpyridinium perchlorate (2). In this case, a 5-fold increase in the quantum yield of fluorescence was observed.

On the other hand, Glasbeek and co-workers have experimentally found that the mechanism of relaxation of excited styryl dyes is determined by rotations around single C–C bonds and only restrictions, imposed simultaneously on all rotations, result in a considerable increase of fluorescence. Therefore, the typical structure of the host–guest complexes in the ground state obviously has no effect on fluorescence, which contradicts the experimental results. This contradiction can be removed if we assume that upon photoexcitation, there is a pronounced shift of the electroni-
It may be implied that such supramolecular systems have an interesting relaxation mechanism of electronically excited states on picoseconds time scale. However, ultrafast dynamics of photocontrolled CB complexes is still largely unexplored. Trying to fill this knowledge gap, we present here our experimental results obtained over recent years on the ultrafast relaxation dynamics of excited host–guest complexes between cucurbiturils and styryl dyes as a representative fluorophore family. In addition, we outline a simple model that allows the estimation of the characteristic time of the restructuring of inclusion complexes upon photoexcitation.

RESULTS AND DISCUSSION

Photophysical Properties of Styryl Dyes. These are heterocyclic organic species that have been extensively studied owing to their applications in high-tech fields, e.g., fluorescent labeling, applications based on nonlinear optical properties, chemosensors, organic light emitting diodes, photochemical applications, laser dyes, etc. (for review, see ref 6). In particular, styryl dye 2-(4-(dimethylamino)styryl)-1-methylpyridinium iodide (close analogue of 1) selectively stains the mitochondria in living cells so that the membrane potential of the mitochondria can be measured by its fluorescence.7

The well-characterized styryl dye cations, whose chemical structure is shown in Figure 1, are able to produce a stable 1:1 inclusion complex with cucurbiturils of appropriate size. Figure 3 shows typical steady-state absorption and fluorescence spectra of 1, as a representative example, in the presence of one equivalent of CB[6] and without it.8 The addition of CB[6] decreases the amplitude of the absorption peak at 450 nm, as its position and half-width are not varied. On doing so, the peak of fluorescence shifts to a blue spectral region by approximately 25 nm and its half-width insignificantly decreases; the peak of fluorescence increases 270 times, which clearly points to the production of the inclusion complexes. Upon the formation of 1:1 host–guest complexes, the fluorescence of 2 increases by 12.6 times in the case of CB[6] and 1.3 times in complexes with CB[8]. The binding constant of 2 with CB[6] has been determined to be $1.1 \times 10^5$ M$^{-1}$. The addition of CB[5] does not lead to any change in the photophysical properties of a solution of 2, indicating the absence of complexes between CB[5] and 2.9

The electronically excited state of styryl dyes in water is strongly quenched. The fluorescence quantum yield of the aqueous solution of 2 is 2.6%,4 while that of 2-4-

(diphenylamino)phenyl-ethenyl-1-methylpyridinium iodide (close analogue of 1) is about 0.03–0.05 %.10,11

A peculiar property of styryl cations is that they are dipolar $A^+–\pi–D$ systems, where the pyridinium unit $A^+$, electron acceptor, and dimethylaminophenyl $D$, electron donor, are linked by a $\pi$-electron conjugated bridge.12 It is well known that the positive charge, which is mainly localized on the acceptor pyridinium group in the ground state, moves toward the dimethylamino donor group upon excitation.13 In the case of 1, it is shown by semiempirical calculations that in the ground state, the positive charge of +0.968e is concentrated mostly on methyl pyridinium moiety, while the N,N-dimethyl aniline moiety has got a positive charge of +0.192e. Upon excitation, it is shown that the positive charge decreases on methyl pyridinium moiety from +0.968e to +0.631e, whereas it increased on N,N-dimethyl aniline moiety from +0.192e to +0.686e. Recently, Chernikova and co-workers14 have calculated that the value of the charge transferred from benzene to pyridinium group is 0.33e for the azacrown-containing styryl dye, which is a close analogue of 1.

Photoinduced charge transfer can provide the possibility for the styryl dye cation to move inside the cucurbituril cavity, complicating the fast dynamics of electronically excited inclusion complexes. Thus, let us consider a simple physically clear model of this interesting feature.

Simple Theoretical Model. We will consider a common structure of the ground state of host–guest complexes in which the charged pyridinium moiety is located inside the cavity as...
another part of dye is outside of it. Upon photoexcitation of guest dyes, intramolecular charge transfer (ICT) occurs and guests can be embedded deeper in the cavity.

To model the displacement of guest species inside the cavity, let us consider an immobile negatively charged circle, which is placed at the origin of the coordinates on the $z$-$y$-plane, and a point positive charge that can move along $x$-axis (see Figure 4).

![Figure 4. Electrostatic interaction between a circle of radius $a$ with charge $q$ and a point charge $e$ (see the explanation in the text).](image)

This system simulates the interaction of negatively charged portal of CB with the positive charge of styryl dye. In equilibrium, the point charge of the pyridinium group is placed at the origin of the coordinates. Upon photoexcitation, a rapid redistribution of electron density occurs and the positive charge passes to the toluene group; in other words, at $x_0$ point out of the $z$-$y$-plane. This leads to a significant increase in the potential energy of the system. In the course of relaxation that follows photoexcitation, the positive charge, rigidly connected with the molecular frame of the dye, returns to the zero position.

The potential energy of the circle with a negative charge of $q$ and a mobile positive charge $e$ as a function of the distance from the center of the circle along the $x$-axis is

$$U = -\frac{qe}{\varepsilon a}\frac{1}{\sqrt{1 + \left(\frac{x}{a}\right)^2}}$$  \hspace{1cm} (1)

Here, $\varepsilon$ is the dielectric constant of the media and $a$ is the radius of the circle.

Hence, the total energy of the system

$$E = \frac{m x^2}{2} + U(x) = U(x_0)$$  \hspace{1cm} (2)

where $m$ is the mass of the point charge that is equal to the mass of the dye particle.

From eqs 1 and 2, it follows

$$\frac{m x^2}{2} = -\frac{qe}{\varepsilon a} \left[\frac{1}{\sqrt{1 + \left(\frac{x}{a}\right)^2}} - \frac{1}{\sqrt{1 + \left(\frac{x_0}{a}\right)^2}}\right]$$  \hspace{1cm} (3)

Assuming that $x/a < 1$ and expanding eq 3 in series in terms of this small parameter, we obtain

$$x^2 = \frac{qe}{\varepsilon ma^3} (x_0^2 - x^2)$$  \hspace{1cm} (4)

From eq 4, it follows

$$dt = -\sqrt{\frac{\varepsilon ma^3}{qe}} \frac{d(x/x_0)}{\sqrt{1 - (x/x_0)^2}}$$  \hspace{1cm} (5)

and the time take by the positive charge to reach the origin of the coordinate from point $x_0$ is expressed by the formula

$$T = -\sqrt{\frac{\varepsilon ma^3}{qe}} \int_{x_0}^{0} \frac{d(x/x_0)}{\sqrt{1 - (x/x_0)^2}}$$  \hspace{1cm} (6)

Taking into account that $\int_0^1 \frac{du}{\sqrt{1-u^2}} = \frac{\pi}{2}$ is a known integral, we finally obtain

$$T = \frac{\pi}{2} \sqrt{\frac{\varepsilon ma^3}{qe}}$$  \hspace{1cm} (7)

Taking physically reasonable values of $a \approx 2 \text{ Å}$, $\varepsilon \approx 10^2$, $m = 200 \text{ a.e.}$, and $q$ is of order of $e$, which is equal to the charge of electron, we have obtained $T \approx 500 \text{ fs}$. Viscosity, which has not been taken into account, obviously increases the value of $T$ so that it is a lower bound for the time taken for deeper embedding into the cavity. In other words, the processes associated with the structural changes of inclusion complexes between cucurbiturils and styryl dyes are on the picosecond time scale. To study the relaxation of the electronically excited states on the picosecond time scale, it is common to use a time-resolved fluorescence up-conversion technique; in our case, the experimental setup was based on a Cr-Forsterite laser that generates pulses of 90 fs with a repetition rate of 96 MHz (pulse energy of 7 nJ) at a fundamental wavelength of about 1250 nm.

**Ultrafast Kinetics of Electronically Excited Host–Guest Complexes between Cucurbiturils and Styryl Dyes.** The time-resolved relaxation of the electronically excited states of styryl dyes has been studied in detail (see refs 5, 18–20 and the references herein) and is usually considered in terms of the model depicted in Figure 5. The

![Figure 5. Schematic plot of the potential energies of styryl dyes versus the reaction coordinate (see discussion in the text).](image)

Frank–Condon state (FC) of the first excited state $S_1$ is created when the trans-form of the ground state $S_0$ of styryl dyes is excited by light. The subsequent relaxation can be considered as a downhill motion of the representative point along a one-dimensional profile of the potential energy of the system. The initial stage, which is associated with vibrational cooling and intramolecular charge transfer (ICT), occurs within a few hundreds of femtoseconds. It is accompanied by a considerable change in the dipole moment of the dye molecule. This change leads to the reorganization of the solvation shell on a picosecond time scale, as well as to the significant diminution of the potential energy of the system. Having an approximately planar structure at this phase of relaxation, the dye fluoresces at wavelengths that become
longer, while the potential energy of the $S_1$ state diminishes and that of the $S_0$ state grows simultaneously. Intramolecular rotary motions of styryl dye determine a slower relaxation stage. They include isomerization around a double bond and rotation around either single bonds in the C–C=C–C fragment. The single-bond rotation results in the so-called twisted intramolecular charge transfer (TICT) state that corresponds to the minimum energy $S_1$. It also plays the role of a nonradiative “sink” region, the conical intersection (CI). A characteristic time of internal conversion via CI is about 100 fs. The CI region can be reached from the fluorescent ICT state over a low-energy barrier that strongly quenches the fluorescence. Thus, there are three characteristic decay times: the first is of the order of hundred femtoseconds, the second of about 1 ps, and the third of tens ps. One may expect that this scheme is also applicable to describing the photophysics of the host–guest complexes of styryl dyes with cucurbiturils that is confirmed by the experiment.

The production of inclusion complexes with CB[n] ($n=6,7$) changes the longest decay time $\tau_3$ from ca. 50 ps for free $2$ to 100–200 ps for bound $2$ in agreement with the observed enhancement of the steady-state fluorescence. As mentioned above, to increase the fluorescence of guest species, the cavity should significantly slow down all intramolecular rotations of the dye in the excited state that cannot be provided by the complex structure in the ground state. This means that after photoexcitation, styryl dye penetrates deeper into the cavity of cucurbiturils, increasing the potential barrier between the ICT and TICT states. The movement inside the cavity is caused by a Coulombic interaction of the negatively charged portals of the cavity and the positively charged dye. The characteristic time of such a shift has been estimated to be about 1 ps (see issue 3). Such a structural reorganization of the inclusion complexes with CB[6] is in agreement with the NMR data obtained by Li and co-workers. They showed that the protonation of the ground state of $1$, when the amino group becomes positively charged, which to some extent plays a role similar to the photoinduced charge transfer, the aniline ring shifts to the CB[6] cavity. It is worth noting that the inclusion complex of $1$ with CB[6] acts by definition as a molecular machine (switch); that is, it is a supramolecular system with a mechanical motion of considerable amplitude that can be caused by various stimuli (for example, light). The same conclusion was reached by Chernikova and co-workers when they studied the inclusion complexes between CB[7] and styryl (pyridinium) dyes that are close analogue of $1$.

Components with a short decay time $\tau_1$ of 100–200 fs, which is associated with vibrational cooling, disappear in the blue region of the fluorescence band of both nonbound and bound $1$. In the red region of the fluorescence band, the components arise with approximately the same time constants that are clearly seen in Figures 6 and 7.

The characteristic time of hydration is about 2 ps, which is determined by the rotary motion of the water molecules in the dye hydration shell, which should be modified by the production of inclusion complexes between CB[n] and styryl dye. According to the above estimation made in issue 3, to get a structural equilibrium, the excited complex needs the time $\tau_2$, whose value may overlap with other characteristic times of the system. To understand the mechanism of such a supramolecular solvation in a more quantitative sense, we have studied the time-dependent fluorescence Stokes shift on a picosecond time scale.

Time-resolved emission spectra were derived from a set of emission decays (see Figures 6 and 7) taken at selected wavelengths according to a procedure that was first described by Maroncelli and Fleming.

Figures 8 and 9 depict the representative spectral reconstructions for instantaneous spectra of aqueous solution of $1$ and its complexes with CB[6] as two-dimensional (2D) fluorescence function in the range of 5 ps. The dependence of the wave numbers, which are related to the fluorescence maxima, on time is indicated by black circles. The temporal transformation of the dye hydration shell demonstrates itself in the continuous red shift of the fluorescence spectrum that is clearly seen in Figures 8 and 9. The solvation involves primarily a libration motion of water molecules and displacement of CB[6], if it is present in solution. The time dependence of the Stokes shift is commonly described by the solvation time correlation function

$$S(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}$$

where $\nu(0), \nu(\infty)$, and $\nu(t)$ are the wave numbers of the maxima of the emission spectra at $t = 0, t \to \infty$ when the system is in equilibrium, and at an intermediate time $t$. Since the aim of this work is to elucidate the kinetics of excited inclusion complexes, ultrafast components that correspond to an inertial response of solvent are not necessary to resolve.
This simplifies the task because a poorly determined value of \( \nu(0) \) is not required.

The evolution of the maxima of the fluorescence spectra, which are shown as black circles in Figures 8 and 9, fits to eq 9, which is obtained from eq 8

\[
\nu(t) = \alpha_1 e^{-t/\tau_1} + \alpha_2 e^{-t/\tau_2} + \nu(\infty) \tag{9}
\]

In Table 1, there are results of this fitting. It is worth noting that the values \( \nu(\infty) \) are in good agreement with the maxima wavelengths of the steady-state fluorescence spectra. Shorter solvation times can be attributed to vibrational cooling, while longer ones can be attributed to the rotation of water molecules in the first hydration shell of 1. The addition of CB[6] results in change of \( \tau_2 \) from 0.81 ps for nonbound 1 to 1.15 ps for the bound dye that is associated with the rotary motion of water molecules in the solvation shell. The value of \( \tau_1 \), which can be attributed to the vibrational cooling, changed from 118 to 224 fs when CB[6] is added in the aqueous solution of 1.

It can be rationalized as follows. The rigid hydrophobic cavity of cucurbiturils has low polarizability, so it cannot considerably change the dye solvation energy as compared to the influence of polar water molecules in the first hydration shell. The cucurbituril cavity seems to play the role of the second hydrophobic solvation shell that affects the first hydrophilic one. Inside the CB[6] cavity, rigorous restrictions are imposed on the intramolecular rotations of styryl dye, and on the liberation of polar water molecules in the first hydration shell. In addition, CB[6] can disturb the hydrogen-bond network around the dye. An observed increase in a shorter solvation time may be related to the well-known fact that a dense network of hydrogen bonds accelerates vibrational cooling.\(^{40}\) It is worth noting that a value of a hypsochromic shift of the steady-state fluorescence, caused by complexation, is about 2.3 kcal/mol, which is in good agreement with the free energy of the H-bond dissociation.\(^{29}\) Therefore, CB[6] destroys the H-bond net, increasing the energy of the system.

Having replaced water by heavy water, we found\(^{31}\) that the 580 nm maximum of the steady-state fluorescence spectra of 1 in the complex is independent of the solvent, whereas the maximum of free 1 at 603 nm in H\(_2\)O shifts to 610 nm in D\(_2\)O. The fluorescence quantum yield increases insignificantly, by 6\% for the free dye and 15\% for its complex with cucurbituril; i.e., a weak normal isotope effect according to the accessed terminology\(^{32}\) was observed. This indicates that the rate of nonradiative processes competing with fluorescence is almost independent of the solvent type. Within the framework of the simple model mentioned above, \( \tau_1 \) in the order of magnitude of 100 fs can be assigned to the vibrational cooling, which is obtained from eq 8

| solvent | solvate | \( \alpha_1 \) | \( \nu(\infty) \) (cm\(^{-1}\)) | \( \nu(\infty) \) (cm\(^{-1}\)) | \( \nu(\infty) \) (cm\(^{-1}\)) |
|---------|---------|----------------|----------------|----------------|----------------|
| H\(_2\)O | 1       | 64 ± 3         | 121 ± 7        | 769 ± 82       | 799 ± 20       | 16415 ± 2   |
|         | 1 + CB[6]| 1523 ± 47      | 223 ± 7        | 424 ± 12       | 1149 ± 28      | 17198 ± 3   |
| D\(_2\)O| 1       | 1537 ± 144     | 288 ± 31       | 731 ± 65       | 1211 ± 80      | 16425 ± 4   |
|         | 1 + CB[6]| 2279 ± 119     | 301 ± 21       | 455 ± 20       | 1630 ± 148     | 17230 ± 4   |

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cucurbiturils. The increase in $\tau_2$ from 799 to 1149 fs by replacing H$_2$O with D$_2$O can be attributed to a higher degree of structuring and viscosity of D$_2$O than those of H$_2$O. The presence of CB[6] in the solution substantially increases $\tau_2$ in comparison with pure solvent (Table 1). This increase can be accounted for by the fact that the formation of the metastable fluorescence state involves the translational movement of the dye solvate in the cavity, where the local viscosity seems to be substantially higher than the viscosity in the free solvent. In addition, the transferred solvate mass is evidently higher for D$_2$O thereby leading to an increase in $\tau_2$ in comparison with H$_2$O.

It is should be noted that within the molecular machine concept, this time can be considered as a molecular switch actuation time. In other words, the time required for the electronically excited styryl dye 1 to move inside the CB6 cavity is approximately 1.1 ps in water and 1.6 ps in heavy water.

**Fluorescence Anisotropy of Inclusion Complexes.** To shed light on the photoinduced movement of dye molecules in cucurbiturils, we have measured the temporal fluorescence anisotropy of such supramolecular systems.

By definition, the fluorescence anisotropy is as follows

$$r = \frac{I_0 - I_\perp}{I_0 + 2I_\parallel}$$

(10)

here, $I_\parallel$ and $I_\perp$ are the fluorescence intensities measured in parallel and crossed directions of the analyzer relative to the linear polarized exciting pulse, respectively. For species having the form close to that of an elongated ellipsoid, which corresponds to 1, the kinetics of the fluorescence anisotropy decay, caused by rotational diffusion, is described by a single time constant and depends on the solvent viscosity $\eta$ and the volume of the fluorophore complex with its close environment $V$.

$$r(t) = r_0 \exp \left( -\frac{t}{\phi} \right)$$

(11)

where $\phi = \frac{\eta V}{kT}$ is the rotational correlation time of the fluorophore, which is determined by the rotational diffusion of the fluorescing complex (solvate). Here, $k$ is the Boltzmann constant and $T$ is the absolute solution temperature. From the relation $r = r(t)$ according to eq 11, a characteristic lifetime of $\phi \approx 207$ ps was found for host–guest complexes and that of $\phi \approx 84$ ps for the free dye. These results agree satisfactorily with the data obtained under the steady-state conditions.

The value of $r_0$ is determined by faster structural changes in the solvate

$$r_0 = \frac{2}{5} \left( \frac{3 \cos^2 \beta - 1}{2} \right)$$

(12)

here, $\beta$ is the angle between the absorbing and emitting solvate oscillators. From eq 12, it follows that the highest value of anisotropy is 0.4 if the absorbing and emitting oscillators are parallel, with an average value of 0.39−0.37. Note that the anisotropy becomes 0.38 when this angle is about 11°. On the subpicosecond time scale, the rotation of the molecules relative to the laboratory coordinate system can be neglected, and the anisotropy measurements may give insight into the intramolecular processes or the relaxation processes associated with the close solvation environment.

Figure 10 shows the anisotropy dependence curves $r = r(t)$ for 1 in water, ethylene glycol, and complexes with CB[6] on the time scale of up to 2.5 ps. Time dependence curves for the total fluorescence intensity $I = I_\parallel + 2I_\perp$ are also shown in the figure. The anisotropy $r = r(t)$ reaches an almost limiting value of $r \approx 0.38$ after no more than 500 fs of fluorescence excitation and remains constant for the dye in ethylene glycol or in complex with CB[6] and slightly decreases in the aqueous solution. For times shorter than 500 fs, almost the same behavior of fluorescence anisotropy was observed for all the samples. The accuracy of the measurements on this time scale does not allow obtaining more detailed information on the dynamics of anisotropy.

In view of these findings, it can be argued that the dye environment in the aqueous solution in the presence of CB[6] is more alike to the viscous solvation shell in ethylene glycol rather than the hydration shell in water. This conclusion confirms the assumption that in the host–guest complex, there is a fast translational displacement of the dye cation into the cavity after excitation by laser pulse.

**CONCLUSIONS**

In this report, we review recent results on the ultrafast relaxation dynamics of electronically excited host–guest complexes of cucurbiturils with pyridinium styryl dyes. Ultrafast fluorescence decays of free dyes and that bound by CB are fitted satisfactorily by the sum of three exponentials. The addition of CB to aqueous solutions of dyes increases the longest relaxation times from about 50 ps for the free dyes to 100−150 ps for the bound ones. This is related to the slowing
down of the intramolecular rotations around the single bonds of the styryl moiety that is caused by guest's displacement inside the cavity. The ultrafast fluorescence depolarization of a styryl dye shows that the displacement is a translational motion along the CB axis. Such movements are caused by electrostatic interaction of a negatively charged CB portal with the guest positive charge that undergoes photoinduced transfer. In fact, such complexes are a molecular machine, the molecular switch.

The fluorescence decays also include components with time constants of about 100 and 1 ps, which are almost independent of complexity. They are associated with vibrational relaxation and supramolecular solvation of the excited state of styryl dyes, respectively. In other words, a longer time is a response time of the photocontrolled molecular machine. It is worth noting that ultrafast dynamics of such type of machines is still largely unexplored and authors hope that this perspective prompts further studies in this field of supramolecular chemistry.

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**Notes**

The authors declare no competing financial interest.

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