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Ultrafast dynamics in the power stroke of a molecular rotary motor

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Light-driven molecular motors convert light into mechanical energy through excited-state reactions. Unidirectional rotary molecular motors based on chiral overcrowded alkenes operate through consecutive photochemical and thermal steps. The thermal (helix inverting) step has been optimized successfully through variations in molecular structure, but much less is known about the photochemical step, which provides power to the motor. Ultimately, controlling the efficiency of molecular motors requires a detailed picture of the molecular dynamics on the excited-state potential energy surface. Here, we characterize the primary events that follow photon absorption by a unidirectional molecular motor using ultrafast fluorescence up-conversion measurements with sub 50 fs time resolution. We observe an extraordinarily fast initial relaxation out of the Franck–Condon region that suggests a barrierless reaction coordinate. This fast molecular motion is shown to be accompanied by the excitation of coherent excited-state structural motion. The implications of these observations for manipulating motor efficiency are discussed.

A detailed understanding of the factors that control the conversion of light into mechanical energy by light-driven molecular machines1,2 is central to their efficient operation. In this work we probe the mechanism of the double-bond photoisomerization that underpins the operation of unidirectional molecular rotary motors, which were first reported by Feringa and co-workers in studies of chiral overcrowded alkenes (Fig. 1)3–5. These molecules comprise a ‘rotor’ (upper part) linked by an ‘axle’ (a double bond in the ground state) to a ‘stator’ (lower part), which may itself be linked to a larger structure, a surface for example6. An excited-state photoisomerization leads to a rotation of the rotor relative to the stator about the axle (the power stroke). The photochemical power stroke is followed by a second slower step in the electronic ground state, a thermal helix inversion, in which the configuration at the stereogenic centre leads to rotation with an overwhelming preference for one direction relative to the stator. A second pair of photochemical and thermal isomerization steps completes the cycle (Fig. 1)7.

The efficiency of the thermal stroke was optimized through chemical synthesis, which has increased the rate by more than a factor of a million, and in principle allows the motors to operate at MHz rotation frequencies7,8. In contrast, rather little is known about the power stroke and how it depends on molecular structure and environment9. Control over this photoisomerization reaction is critical for the future exploitation of light-driven motors in molecular machines and devices. For example, optimization of isomerization over ground-state repopulation maximizes the use of optical power and minimizes the generation of deleterious local heating. To achieve this level of control requires knowledge of both molecular dynamics on the excited-state potential surface and of the coupling between the excited- and ground-state surfaces, which in turn requires measurements of the ultrafast dynamics; such a study is reported here.

One recent study10 of ultrafast transient absorption in a molecular motor concluded that a structural relaxation within 1.7 ps was followed by an excited-state decay of 12 ps, a conclusion that was broadly supported by recent quantum mechanical and molecular dynamics calculations11. Here we apply ultrafast fluorescence up-conversion spectroscopy with a time resolution better than 50 fs (ref. 12) to probe the earliest excited-state dynamics of the molecular motor 1 (Fig. 1). Ultrafast fluorescence spectroscopy is uniquely suited to this objective because it unambiguously reveals information about excited-state dynamics, and preferentially probes the initially excited bright (Franck–Condon) region of the excited-state potential energy surface13. Here we resolve excited-state dynamics on the tens of femtoseconds timescale, and these dynamics are shown to be coupled with coherent low-frequency modes in the excited state. The implications of these observations for controlling the operational efficiency of light-driven motors are considered.

Results and discussion
Time-resolved fluorescence data. Figure 2a shows the electronic spectra for 1 in dichloromethane (DCM). The absorption (maximum at 390 nm) is narrow and well defined and quite characteristic of a substituted fluorene, which suggests the excitation is localized on the stator14. In contrast, the fluorescence spectrum, which is very weak (quantum yield estimated at <10−4), is exceedingly broad, stretching from 350 nm to >750 nm with a maximum at 474 nm. Such a low yield and broad emission are characteristic of a molecule undergoing excited-state structural

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Figure 1 | Structure of the molecular motor 1. The three components, rotor–axle–stator, are indicated and the photochemical (power) and thermal strokes in the operation are shown. Further photoisomerization and thermal isomerization steps complete one cycle of the motor rotation.
The ultrafast (about 100 fs) quenching of fluorescence may occur in the excited state potential surface it is necessary to recover the temporal evolution of the emission spectrum. This is achieved by area normalizing the wavelength-resolved deconvoluted decay functions to the intensity in the time-integrated emission spectrum (Fig. 2a). The resulting spectra are shown in Fig. 3a, where the data points are fitted to a log-normal line shape (complete information is given in Supplementary Section S1 and Figs S1 and S2). As the spectra are much broader than the range that can be accessed by fluorescence up-conversion, the log-normal fits are constrained by assuming that the emission spectral intensity is zero at 350 nm and 800 nm, consistent with the steady-state spectrum (Fig. 2a). The temporal evolution of the fitted spectra is best represented by the contour plot in Fig. 3b. The time-dependent mean frequency, intensity (spectral area) and spectral width are shown in Fig. 3c.

Excited-state dynamics. The dominant feature in the time-dependent excited-state dynamics (Fig. 3) is the non-exponential decay in the integrated fluorescence intensity, which has an ultrafast (about 100 fs) component plus a slower decay on a picosecond timescale. This is accompanied by a continuous shift to lower wavenumber (red shift) of the emission spectra with time (Fig. 3b,c). The spectral shift arises from the ultrafast collapse of the emission on the blue edge of the spectrum (Fig. 2b). No rise time was detected on the red edge, such as that expected if polar solvent reorientation stabilized the excited state (solvation dynamics). Such a solvation red shift is, in any case, expected to be small in the relatively apolar solvent used, and essentially identical kinetics were observed for I in the apolar but more viscous solvent cyclohexane (data not shown). The lack of a viscosity effect is consistent with earlier measurements for which a very high viscosity was required to detect the red edge, such as that expected if polar solvent reorientation stabilized the excited state (solvation dynamics). Such a solvation red shift is, in any case, expected to be small in the relatively apolar solvent used, and essentially identical kinetics were observed for I in the apolar but more viscous solvent cyclohexane (data not shown). The lack of a viscosity effect is consistent with earlier measurements for which a very high viscosity was required to influence the photochemical equilibrium of a molecular motor18. Thus, we conclude that the rapid decay and red shift of the spectrum reflect intrinsic dynamics on the excited-state potential energy surface of the molecular motor rather than solvent dynamics.

The ultrafast (about 100 fs) quenching of fluorescence may occur by one of two mechanisms, both of which involve excited-state structural relaxation. First, the excited state undergoes radiationless
decaying directly back to the ground state, such as may occur through internal conversion at a conical intersection between the ground-state and excited-state potential energy surfaces. For such an ultrafast decay, the conical intersection must be reached via a barrierless structure change. Alternatively, fluorescence may be quenched by structural relaxation on the excited-state surface, in which the population evolves away from the emissive Franck–Condon excited state to a conformation with a low or zero fluorescence-transition moment; this dark (or near-dark) state may then decay to the ground state on a longer timescale. The latter mechanism is more consistent with the observed non-single exponential decay of the integrated fluorescence intensity, where the fast component reflects the light to dark structural evolution and the slower component the rate of radiationless decay of the dark state back to the ground state. A non-exponential population relaxation for the direct-decay mechanism is expected only if there is an initial distribution of ground-state structures.

Wave-packet dynamics. The second notable feature in the time-domain data is the strong oscillation in the time-resolved emission, which is observed in both the time-dependent integrated intensity and the mean frequency of the time-resolved spectrum (Fig. 3b,c). An oscillation in the mean frequency may arise when a Franck–Condon active vibration is displaced between the ground and excited electronic states. Thus, ultrafast electronic excitation launches a wave packet on the excited-state surface that oscillates with the frequency of the mode in the excited state. In this case the phase of the oscillation observed is expected to shift by π when the observation wavelength is changed from the blue to the red edge of the emission spectrum, and its amplitude is expected to be greatest on the rising and falling edges of the spectrum. The oscillation observed in the time-resolved integrated intensity shows that the Franck–Condon active mode must also be coupled to the transition moment; that is, the motion excited in the upper state modulates the probability as well as the energy of fluorescence. In this case the amplitude of the entire spectrum is modulated and there is no phase shift with observation wavelength. Although the very broad emission spectrum (Fig. 2a) precludes fluorescence up-conversion observations across the entire spectrum, within the range of wavelengths investigated an approximately π/2 phase shift is observed as we move across the spectrum (Supplementary Information Table S2). However, the amplitude of the oscillation is significantly stronger around the maximum in the emission spectrum than on the edges. These data suggest that, at least for the dominant lower-frequency mode, the modulation arises both from coupling between the excited-state vibration and the transition moment and from modulation of the frequency of the electronic transition.

Excited-state structural dynamics. To assign the observed ultrafast fluorescence decay and oscillatory dynamics we turn to existing quantum chemical and molecular dynamics simulations of the photoisomerization of carbon–carbon double bonds. These models, which have a long history, typically invoke motion on two coordinates in the excited electronic state, which leads to a conical intersection between the excited and ground electronic states, where ultrafast internal conversion may occur. Calculations reported previously on a motor analogous to I suggested that 6Δσ–6π* electronic excitation is followed by simultaneous twisting about the C9–C1′ double bond and substantial pyramidalization at the stator–axle linkage (C9). We suggest that the experimentally observed oscillations reflect Franck–Condon excitation of the inversion (pyramidalization) mode at C9. Motion along the pyramidalization coordinate coupled with C9–C1′ rotation takes the molecule out of the strongly emissive Franck–Condon region to a point on the potential surface that has a significantly reduced fluorescence-transition moment; the nuclear motions proposed and the relevant potential energy surface are illustrated in Fig. 4. This initial motion leads to the observed ultrafast decay of fluorescence. The molecule then decays from this dark state back to the ground state on a timescale of approximately 1 ps, presumably through an S0–S1 conical intersection. In the earlier calculations on the analogue of I, two conical intersections were identified on the S1 potential energy surface as a function of the twist and pyramidalization coordinates, both lying slightly above the
and Fig. S4) show that the decay of a transient state that is populated
constant, consistent with the decay time of the relaxed excited state
the picosecond timescale.

population decays to the ground state through a conical intersection (CI) on
about the minimum (Min) on the potential surface. This thermalized
approximately 100 fs time constant, which leads to a thermal population
diffuse circle), which leads to the observed 100 fs relaxation. The coherent
takes the population out of the bright Franck–Condon region (shown as a

minimum energy; these ideas are illustrated in Fig. 4b. In this model,
the ultrafast component arises from structural dynamics, which
suggests that the 1.7 ps component reported as structural relaxation
in earlier transient-absorption experiments on a related molecular
motor could be associated with population decay, and the slower
component observed there probably reflects vibrational cooling of
the hot ground state of the molecular motor. Preliminary transient-
absorption studies of 1 reported here (see Supplementary Section S4
and Fig. S4) show that the decay of a transient state that is populated
within a few hundred femtoseconds occurs with a 1.5 ± 0.3 ps time
constant, consistent with the decay time of the relaxed excited state
seen in fluorescence. The earlier calculations on an analogue of 1
mentioned above suggested that the relaxed state is already
substantially distorted compared with the Franck–Condon state
(Fig. 4a), which suggests that extensive structural change has already
occurred in the excited state.

Although the qualitative agreement between the calculations
and the experiment is good, the assignment of the 113 cm⁻¹ mode
to the inversion/pyramidalization coordinate remains speculative.
However, there is additional evidence from the damping constants
that this mode is involved actively in the primary isomerization
(power) stroke of the molecular motor. This low-frequency mode is
damped on the sub 100 fs timescale, which is as fast as or faster
than the relaxation out of the Franck–Condon region. This is in
contrast to the weaker 180 cm⁻¹ mode, which has a much longer
damping time, suggesting that the latter may simply be a spectator
mode, uninvolved in the excited-state dynamics.

We have sought a more definitive assignment of these coherent
excited-state modes through resonance Raman spectroscopy
(Fig. 5). Although continuous-wave Raman spectroscopy (unlike
time-resolved fluorescence) can only yield ground-state frequencies,
the observation of a resonance enhancement does reveal modes that
are coupled to the optical excitation, and thus points to nuclear
motions that are displaced from equilibrium geometry along
normal coordinates in the excited state. The resonance Raman
spectrum (Fig. 5) does not show modes in the ground state that
match exactly the observations in the excited state (Fig. 2b). This
is not in itself surprising. It is not, in general, possible to find a direct
one-to-one correspondence between ground- and excited-state
frequencies, as the widely studied example of cis-stilbene, which
also undergoes a fast excited-state reaction believed to involve both
twisting and pyramidalization, shows. However, resonantly
enhanced modes near 300 cm⁻¹ are observed, one of which is
calculated in the present study to involve out-of-plane nuclear
displacement around C9 (Fig. 5). It is plausible that such modes are
down shifted in frequency in the excited electronic state
following a π–π⁺ transition localized at the C9 axle double bond.

The observation of optically excited strongly damped coherent
excited-state dynamics is of potential importance to the operation
of light-driven molecular motors. That there is room for further
optimization of the motor operation is evident from quantum-
yield data (Supplementary Section S5 and Fig. S6), which show a
yield of 0.14. First, the important role for the inversion mode at C9 in the structural dynamics is suggested by both experiment and theory, so synthetic strategies that modulate the electronic structure in the C9–C1′ double bond probably modify the efficiency of operation; we are currently studying a series of derivatives of 1 to further probe this dependence. Second, the observation of coherent dynamics in a mode that is involved actively in the excited-state reaction coordinate raises the possibility that coherent control schemes can be exploited to drive the reaction in a specific direction. A change in the control of photochemical reactivity using chirped pulses was discussed in a number of cases, which include a theory-based proposal for molecular motors and an experimental demonstration on the biological photoswitch in the retinal visual pigment bacteriorhodopsin. However, its application has proved to be limited to very few examples, because of both the ultrafast dephasing times characteristic of electronic states in fluid media at room temperature and the difficulty of optically accessing the chemically important modes. The present data suggest that coherent excitation schemes could be applied to control the reaction of light-driven molecular motors, at least on the sub 100 fs timescale of the dephasing time associated with the active mode. Within this limitation, appropriately shaped pulses could be used to steer the excited state towards (or away from) the conical intersection, and thus optically control the efficiency of motor rotation.

Methods

A titanium sapphire laser that delivered 18 fs pulses at 800 nm with an 80 MHz repetition rate was used, and the two frequencies required by the experiment were obtained through second-harmonic generation. The ultrafast up-conversion apparatus is described in detail elsewhere. Essentially, up-conversion is an ultrafast sampling method in which solute fluorescence excited by an ultrashort 400 nm pulse is focused and up-converted solvent absorption is presented in the Supplementary Information. Further experimental information on Raman and transient electronic spectroscopy, J.C. and I.H. analysed the time-resolved data, A.C. performed the time-resolved experiments, I.H. constructed the up-conversion apparatus, W.R.B obtained and analysed the Raman data, and S.R.M. wrote the paper and all the authors commented and contributed to the writing of the manuscript.

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Author contributions

S.R.M., B.L.F. and W.R.B conceived and designed the experiments. J.C. and K.A. performed the time-resolved experiments, I.H. constructed the up-conversion apparatus, A.C. and B.L.F designed and synthesized I and J.C. and A.C. performed the steady-state electronic spectroscopy, J.C. and I.H. analysed the time-resolved data, A.C. performed the density functional theory calculations, W.R.B obtained and analysed the Raman data. S.R.M. wrote the paper and all the authors commented and contributed to the writing of the manuscript.

Additional information

The authors declare no competing financial interests. Supplementary information and chemical compound information accompany this paper at www.nature.com/naturechemistry. Reprints and permission information is available online at http://www.nature.com/reprints. Correspondence and requests for materials should be addressed to B.L.F. and S.R.M.