Toward Fast and Efficient Visible-Light-Driven Molecular Motors: A Minimal Design

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A key goal in the development of light-driven rotary molecular motors is to facilitate their usage in biology and medicine by shifting the required irradiation wavelengths from the UV regime to the nondestructive visible regime. Although some progress has been made toward this goal, most available visible-light-driven motors either have relatively low quantum yields or require that thermal steps follow the photoisomerizations that underlie the rotary motion. Here, a minimal design for visible-light-driven motors without these drawbacks is presented and evaluated on the basis of state-of-the-art quantum chemical calculations and molecular dynamics simulations. The design, featuring dihydroxyridinium and cyclohexenylidene motifs and comprising only five conjugated double bonds, is found to produce a full 360° rotation through fast photoisomerizations (excited-state lifetimes of \(\approx 170-250\) fs) powered by photons with energies well below 3 eV.

1. Introduction

Molecular motors are molecules with the ability to produce directed mechanical motion by using energy from an external source. Among various types of synthetic molecular motors available today, those that achieve 360° unidirectional rotary motion through the absorption of UV or visible light are commonly known as light-driven rotary molecular motors.[17–25] Typically, the clockwise (CW) or counterclockwise (CCW)—as determined by the molecular chirality—rotation motion results from consecutive \(E \rightarrow Z\) and \(Z \rightarrow E\) photoisomerizations around a carbon–carbon double bond that connects two distinct molecular halves. Furthermore, for most motors of this type (but not all[26]) the reaction cycles also include slower thermal conformational relaxation steps.

The first synthetic light-driven rotary molecular motors, based on sterically overcrowded alkenes, were developed in the late 1990s[27] and have subsequently attracted considerable interest, both in terms of improving the performance of these motors[28–38] and in exploiting the mechanical motion that they produce for useful applications.[39–45] Under ambient conditions, the intrinsic rotational frequencies attainable by freely floating (in solution) overcrowded-alkene motors are limited in two different ways. First, the thermal steps of the reaction cycles are not as fast as the photoisomerizations around the central carbon–carbon double bond that power the motors.[28,34] Second, the photoisomerization quantum yields (QYs) do not exceed 20–30% because of the coupling of the desired torsional motion to an undesirable pyramidalization of one of the central carbon atoms.[34,35,46,47] From the point of view of applications, adding to these challenges is the fact that most overcrowded-alkene motors are driven by energetic UV light, which is more damaging to the motors and their environment than visible light. Thus, a key goal in the development of light-driven molecular motors is to make them responsive to visible light,[22,25,48–52] so as to facilitate their usage in biological systems and other soft materials.[53]

Against this background, considerable efforts have been devoted both to finding ways to accelerate the thermal steps of overcrowded-alkene motors[26–30,33–38,54–57] and to put forth alternative light-driven motor designs that require no thermal steps to complete a full 360° rotation.[21,58–60] Furthermore, progress has also been made in the design of new motors with photoisomerization QYs that are less hampered by pyramidalization at the isomerizing bond than overcrowded-alkene motors.[47,61–63] For example, it has been found that it is possible to hinder the pyramidalization in motors that incorporate a protonated or alkylated nitrogen Schiff base,[47] thanks to the electron-withdrawing capability of the cationic nitrogen center, whereby both high QYs and short excited-state lifetimes become attainable.[61,62] Moreover, a strategy to reach this goal even in the absence of a cationic moiety has been proposed, where the pyramidalization is rather curbed by enabling part of the motor to become aromatic in the photoactive excited state.[63] The challenge to develop visible-light-driven motors, on the other hand, has started to be met only recently (see Scheme 1).

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For example, following an early (in 2003) design that utilized push–pull substituents to make an overcrowded-alkene motor (compound I in Scheme 1) operable by $\lambda = 430$ nm light[64] it has been shown that the use of a palladium–tetraphenylporphyrin (compound II in Scheme 1) or a ruthenium(II)–bipyridine (compound III in Scheme 1) complex as a photosensitizer allows overcrowded-alkene motors to be driven by $\lambda = 530–550$ and 450 nm light, respectively.[55,56] In a different approach, the extension of the aromatic core of one such motor yielded a motor (compound IV in Scheme 1) that similarly can be operated by light up to $\lambda = 490$ nm.[52] As for other motor designs, Dube and co-workers[22,26] devised a hemithioindigo-based motor (compound V in Scheme 1) functioning with light up to $\lambda = 500$ nm, whereas Lehn and co-workers[21] introduced camphorquinone-derived imine motors (compound VI in Scheme 1) involving only photochemical steps fueled by UV or visible light.

In this work, we propose a minimal design of molecular motors that not only are powered by visible light, but whose $E\rightarrow Z$ and $Z\rightarrow E$ photoisomerizations are also fast, efficient, and yielding 360° unidirectional rotary motion without intermediary thermal steps. In particular, by performing quantum chemical calculations and nonadiabatic molecular dynamics (NAMD) simulations[66–72] in the framework of complete active space self-consistent field (CASSCF) theory,[15,16] we predict that visible-light-driven motors can be devised in a straightforward way by extending the $\pi$ conjugation of UV-powered Schiff-base motors from three to five double bonds. Furthermore, importantly, we show that this can be done without compromising the speed and efficiency with which the photoisomerizations of the Schiff-base motors occur.[21,62] For the purpose of the study, the UV-powered Schiff-base motor pictured in Scheme 2 and designed in our recent computational work[62] is used as one (out of four, see below) reference system. This system, which features a pyrroline motif connected by an olefinic bond to a cyclohexenylidene motif, is hereafter referred to as motor 1a.

### 2. Results and Discussion

#### 2.1. Motors Considered in this Work

Whereas 1a, through minimum energy path (MEP) calculations and NAMD simulations, has been found to produce 360° unidirectional rotary motion in a purely photochemical fashion,[62] it is worth pointing out that this is achieved despite the absence of a stereocenter in this motor. Instead, the CW or CCW direction of the $E\rightarrow Z$ and $Z\rightarrow E$ photoisomerizations around the central olefinic bond is, as shown by the MEP and NAMD data,[52] controlled by the asymmetry introduced by the ring-puckered cyclohexenylidene unit. Specifically, the $E$ and $Z$ isomers of 1a have two possible orientations of the 5’-carbon atom relative to the approximate plane formed by the other carbon atoms of the cyclohexenylidene moiety: outward (out) and inward (in). Accordingly, there are four different isomers of 1a that can be labeled 1a-Eout, 1a-Ein, 1a-Zout, and 1a-Zin (see Scheme 2). Because of this out/in orientation of the 5’-carbon atom, the 1a-Eout and 1a-Zout pair of isomers complete a full 360° CCW rotation through consecutive $E\rightarrow Z$ and $Z\rightarrow E$ photoisomerizations, whereas the 1a-Ein and 1a-Zin pair conversely complete a full 360° CW rotation.[52]

As the four isomers of 1a form two pairs of axially chiral enantiomers, 1a-Eout/1a-Ein and 1a-Zout/1a-Zin, the thermal free-energy barriers separating the $E_{\text{out}}$ and $E_{\text{in}}$ and the $Z_{\text{out}}$ and $Z_{\text{in}}$ enantiomers need to be sufficiently large for this motor design to be successful. Indeed, if this is not the case, it will be difficult to isolate an enantiopure out/in isomer. Additionally, asymmetric synthesis techniques such as dynamic kinetic resolution[75,76] and, hence, to control the direction of photoinduced rotation. Thus, it is of interest to explore ways to increase the enantiomerization barriers as much as possible. In this work, we investigate the possibility that these barriers can be increased by introducing substituents bulkier than a hydrogen atom at the 4’,5’-positions of the cyclohexenylidene, based on the idea that such substituents may exert steric hindrance for the enantiomerizations (an alternative strategy would have been to bridge the cyclohexenylidene, as in α-pinene[77]). To this end, motors with the 4’ and 5’ hydrogen atoms (R=H) replaced by methyl groups, chlorine atoms, or bromine atoms were also considered, as shown in Scheme 3. The resulting motors, which together with 1a constitute the reference systems for our study, are denoted 1b (R=Me), 1c (R=Cl), and 1d (R=Br).

To redshift the excitation wavelengths of 1a–d toward the visible regime, three different approaches to extend the $\pi$ conjugation were considered, as illustrated in Scheme 3. In the
first approach, a vinyl group is added to the 3’-position of 1a–d to yield motor candidates 2a–d, respectively. In the second approach, the pyrrolinium motif of 1a–d is replaced by a dihydropyridinium motif, resulting in motor candidates 3a–d. In the third approach, finally, the structural alterations in 2a–d and 3a–d are combined to give motor candidates 4a–d, with a total of five conjugated double bonds (compared to three and four such bonds in 1a–d and 2a–d/3a–d, respectively).

2.2. Light-Absorption Features

First, the light absorption of all motors was investigated by calculating their lowest two excited singlet states (S1 and S2) by using both complete active space second-order perturbation theory (CASPT2)[80] and the approximate coupled-cluster singles and doubles (CC2) method.[81] As further described in the Supporting Information, the calculations were done with the cc-pVTZ basis set,[80] based on ground-state (S0) geometries optimized with the CASSCF method or with Møller–Plesset second-order perturbation theory (MP2). The CASPT2 calculations were performed with active spaces comprising the full π systems of the motors, that is, by utilizing CAS(6,6), CAS(8,8), and CAS(10,10) for 1a–d, 2a–d/3a–d, and 4a–d, respectively.

The full results of the calculations are summarized in Tables S2 (CC2 data) and S3 (CASPT2 data) of the Supporting Information, which show that S1 is consistently the bright and photoactive ππ* state characteristic of protonated Schiff bases[81] and that this state is well separated from S0 in most cases by more than 1 eV. Trends in the vertical S0→S1 excitation energies of the Eout and Ein isomers of the motors are highlighted in Figure 1 (being enantiomers, the Eout and Ein data sets are identical), whereas the corresponding trends for the Zout and Zen isomers are shown in Figure S2. As the latter trends are analogous to the former trends, the discussion below is focused on the Eout and Ein isomers.

From the parallel curves in Figure 1, it can first be concluded that the CASPT2 and CC2 predictions as to how the energy of the photoactive S1 state varies between the motors are very similar. Thus, for the present purposes, it suffices to discuss the CASPT2 results. Furthermore, focusing on these energies is sensible in that they throughout lie above the CC2 energies. Therefore, any CASPT2-based conclusion regarding the possibility to bring the light absorption into the visible regime below 3.1 eV is also supported by the CC2 data.

Starting with reference motors 1a–d, the S1 energies in Figure 1 are solidly in the near-UV region, falling between 3.8 and 4.0 eV. However, by adding a vinyl group to the 3’-position to obtain 2a–d, the S1 energies are redshifted by an appreciable 0.5 eV, attaining values between 3.3 and 3.5 eV irrespective of whether the 4’,5’-positions hold H atoms (as in 2a), Me groups (as in 2b), Cl atoms (as in 2c), or Br atoms (as in 2d). Alternatively, even larger redshifts are predicted to arise by replacing the pyrrolinium motif of 1a–d by a dihydropyridinium motif in 3a–d, which lowers the S1 energies to between 3.2 and 3.4 eV. Furthermore, although neither the addition of a vinyl group nor the incorporation of a dihydropyridinium motif is by itself sufficient to reach the visible regime, the two strategies applied together are successful in this regard, as shown by the results for 4a–d. In fact, the combined net effect appears essentially additive, helping redshift the S1 energies by 1.0 eV down to between 2.8 and 3.0 eV for these motors. Accordingly, there appears to be a straightforward route to the design of visible-light-driven motors starting from UV-powered Schiff-base motors. Next, we turn to investigating whether this route may produce motors that are also fast and efficient, starting with an assessment of their enantiomerization barriers.

2.3. Enantiomerization Barriers

As discussed above, the potential of the motor design put forth in this work cannot be fully realized unless the thermal free-energy barriers separating the Eout and Ein and the Zout and Zen enantiomers of the motors are fairly large. Therefore, it is of

Figure 1. Vertical S1→S0 excitation energies of the Eout and Ein isomers of motors a) 1a–4a, b) 1b–4b, c) 1c–4c, and d) 1d–4d in the near-UV (λ < 400 nm, > 3.1 eV) or visible (λ > 400 nm, < 3.1 eV) regime calculated with CASPT2 and CC2.
interest to calculate these barriers, which was done as described in the Supporting Information for all motors in the gas phase and in nonpolar (cyclohexane) and polar (water) solvents by using both MP2 and density functional theory (DFT) methods in combination with the cc-pVTZ basis set. For the DFT calculations, three different functionals were used: B3LYP, M06-2X,[82] and ωB97X-D.[83] From the full results of the calculations summarized in Table S4, it can be seen that the variation between the methods in their estimates of the $E_{\text{out}}\rightarrow E_{\text{in}}$ and $Z_{\text{out}}\rightarrow Z_{\text{in}}$ barriers for any given motor is generally small, in most cases around 5 kJ mol$^{-1}$. Furthermore, the variation in how the barriers are predicted to change from one motor to another, which is our main focus, is naturally even smaller. Thus, for the sake of brevity, Figure 2 highlights the B3LYP/water results for how the $E_{\text{out}}\rightarrow E_{\text{in}}$ barriers vary between the motors (the trends for the corresponding $Z_{\text{out}}\rightarrow Z_{\text{in}}$ barriers are very similar).

From Figure 2, it is clear that there is a steady increase in the enantiomerization barriers when the H atoms at the 4,5'-positions of 1a/2a/3a/4a (barriers of ≈25 kJ mol$^{-1}$) are replaced by bulkier Me groups in 1b/2b/3b/4b (≈40–50 kJ mol$^{-1}$), Cl atoms in 1c/2c/3c/4c (≈60–70 kJ mol$^{-1}$), and Br atoms in 1d/2d/3d/4d (≈70–90 kJ mol$^{-1}$). Hence, invoking the definition that the $E_{\text{out}}/E_{\text{in}}$ and $Z_{\text{out}}/Z_{\text{in}}$ enantiomer barriers are separable if their half-lives are at least 1000 s,[84] especially the Br-substituted systems have enantiomerization barriers of sufficient magnitude for the isolation of enantiopure out/in isomers to be feasible even at room temperature.

2.4. Photochemical Steps

Among the Br-substituted systems 1d/2d/3d/4d, the motor with the longest-wavelength absorption is 4d, whose CASPT2 $S_1$ energies of 2.8 eV fall well within the visible regime (see Figures 1 and 52). Thus, it is of particular interest to assess the speed and efficiency of this motor. To this end, and as further described in the Supporting Information, the $E\rightarrow Z$ and $Z\rightarrow E$ photoisomerizations of 4d were modeled by performing MEP calculations and NAMD simulations by using state-averaged CASSCF (SA-CASSCF) in combination with the cc-pVDZ[85] and SVP[86] basis sets, respectively. For each geometry along the MEPs, dynamic electron correlation effects were accounted for through CASPT2 single-point calculations. Starting from the vertically excited Franck–Condon (FC) points in the photoactive $S_1$ state, the MEPs of the $E_{\text{out}}$, $Z_{\text{out}}$, $E_{\text{in}}$, and $Z_{\text{in}}$ isomers of 4d are presented in Figure 3. For comparison, the corresponding MEPs were also computed for motors 1d/2d/3d. These MEPs, which are very similar to the ones of 4d, are shown in Figures S3–S5.

From Figure 3, it is notable that the excited-state evolution from the FC point is for each isomer of 4d dominated by torsional motion around the central olefinic bond, which is in line with the ability of 4d to function as a rotary motor. Furthermore, the torsional motion is favorably barrierless and brings the systems toward assumed $S_1/S_0$ conical intersection regions, where they can be funneled to the $S_0$ state. For the $E_{\text{out}}$ and $Z_{\text{in}}$ isomers, the direction of motion is such that the values of the $\omega$ dihedral angle (see Scheme 3) are continuously increasing, which is here defined as CCW motion. The $E_{\text{in}}$ and $Z_{\text{out}}$ isomers, conversely, produce CW motion occurring toward decreasing $\omega$ values. These $E_{\text{out}}/Z_{\text{in}}$ and $E_{\text{in}}/Z_{\text{out}}$ pairings of the isomers are further accentuated by the fact that CASSCF $S_2$ geometry optimizations started from the end points of the MEPs yield, by completing net 180° rotations around the central olefinic bond, $Z_{\text{in}}$ as the photoprod of the $E_{\text{out}}$ path and $E_{\text{in}}$ as the photoprod of the $Z_{\text{out}}$ path, and similarly $Z_{\text{out}}$ as the photoprod of the $E_{\text{in}}$ path and $E_{\text{out}}$ as the photoprod of the $Z_{\text{in}}$ path. Accordingly, 4d appears capable of producing 360° unidirectional rotary motion from consecutive $E\rightarrow Z$ and $Z\rightarrow E$ photoisomerizations alone, without intermediary thermal steps, and is able to use the out/in orientation of the $S'$-carbon...
atom to control the direction of rotation—CCW for the $E_{\text{out}}/Z_{\text{in}}$ pair and CW for the $E_{\text{in}}/Z_{\text{out}}$ pair.

Another piece of valuable information from the MEPs is that the $E\rightarrow Z$ and $Z\rightarrow E$ photoisomerizations of 4d proceed almost without any pyramidalization of the central olefinic carbon atoms. Specifically, as revealed by Table S5, the $\alpha$ and $\alpha'$ dihedral angles (see Scheme 3) are consistently of small magnitudes (at most 4°) for all geometries along the MEPs. Given that a much more pronounced pyramidalization is thought to be a key factor in limiting the QYs of overcrowded-alkene motors to 20–30%,[34,35,46,47] one may then expect 4d to show favorable photoisomerization dynamics.

Turning, thus, to the NAMD simulations, these were run for maximally 700 fs and with ten different initial nuclear configurations and velocities for each of the $E_{\text{out}}$, $Z_{\text{in}}$, $E_{\text{in}}$, and $Z_{\text{out}}$ isomers of 4d. Started in the $S_0$ state, the trajectories were allowed to hop to the $S_1$ state on the basis of criteria for the magnitudes of the energy gap and nonadiabatic interactions between the states that are specified in the Supporting Information. Following a previous assessment of the importance of multiple hopping events for the photoisomerization dynamics of Schiff-base motors,[35,40] only one single hop between the $S_1$ and $S_0$ states was allowed for each trajectory. Two key quantities estimated by the simulations are defined in the following way. First, the photoisomerization time (PIT) is defined as the time needed to form the $Z_{\text{in}}$ isomer from the $E_{\text{out}}$ isomer and vice versa (or to form the $Z_{\text{out}}$ isomer from the $E_{\text{in}}$ isomer and vice versa) by completing a net 180° CCW rotation (or a net 180° CW rotation) around the central olefinic bond relative to the initial nuclear configuration. Second, the excited-state lifetime ($\tau$) is defined as the time it takes before a CCW $E_{\text{out}}/Z_{\text{in}}$ or a CW $E_{\text{in}}/Z_{\text{out}}$ trajectory decays to the $S_0$ state. These results from the simulations are listed in Table 1.

From Table 1, it is first encouraging to note that the average $\tau$ and PIT values are small for all isomers of 4d, amounting to only 170–250 fs ($\tau$) and 540–570 fs (PIT) for the $E_{\text{out}}/Z_{\text{in}}$ pair and 190–240 fs ($\tau$) and 540 fs (PIT) for the $E_{\text{in}}/Z_{\text{out}}$ pair. In this respect, 4d compares very favorably to overcrowded-alkene motors, which typically have excited-state lifetimes of 1 ps or more.[35,40] Furthermore, it is actually the case that the values in Table 1 are not far off those previously attributed to UV-powered Schiff-base motors,[31,62] such as the $\tau$ values of 170–190 fs predicted for reference motor 1a through the same type of modeling.[52] Hence, besides establishing a simple route to transform UV-powered Schiff-base motors into visible-light-driven Schiff-base motors, this work also predicts that this can be done without slowing down the photochemical steps, although obtaining quantitatively accurate $\tau$ and PIT values would clearly require that many more than ten NAMD trajectories be run for each of the four isomers.

As for obtaining well-converged and quantitatively accurate estimates of the photoisomerization QYS of 4d, this too would demand calculating a more numerous set of trajectories than deemed affordable herein. Furthermore, a more elaborate treatment of trajectory surface hopping would be needed, such as Tully’s fewest-switches algorithm.[36] Although these are not feasible options, especially at the CAS(10,10) level, Table 1 shows that seven ($E_{\text{out}}$), six ($Z_{\text{in}}$), seven ($E_{\text{in}}$), and four ($Z_{\text{out}}$) trajectories among the ten calculated for each isomer do complete the corresponding photoisomerization within 700 fs. These results suggest that 4d could well attain high photoisomerization QYS. Moreover, similar to the situation for 1a,[62] each isomer of 4d exhibits perfect (100%) directionality in that all reactive photoisomerization trajectories for the isomer in question proceed in one and the same direction.

To illustrate the full 360° rotations achieved by the $E_{\text{out}}/Z_{\text{in}}$ and $E_{\text{in}}/Z_{\text{out}}$ pairs of isomers of 4d, Figure 4 highlights the changes in the $\omega$ dihedral angle along typical photoisomerization trajectories of the different isomers. In addition, two multimedia files in the Supporting Information contain molecular animations of these processes. As can be seen, Figure 4 corroborates the MEP results by showing that the $E\leftrightarrow Z$ and $Z\leftrightarrow E$ photoisomerizations produce 360° unidirectional rotary motion around the central olefinic bond with continuously increasing or decreasing $\omega$ values. Furthermore, the direction of rotation—CCW for the $E_{\text{out}}/Z_{\text{in}}$ pair and CW for the $E_{\text{in}}/Z_{\text{out}}$ pair—is controlled by the out/in orientation of the 5′-carbon atom.

### Table 1. $\tau$ and PIT values for the ten NAMD trajectories calculated for each of the $E_{\text{out}}/Z_{\text{in}}$, $E_{\text{in}}$, and $Z_{\text{out}}$ isomers of motor 4d.

| Trajectory | $\tau$ (fs) | PIT (fs) | $\tau$ (fs) | PIT (fs) | $\tau$ (fs) | PIT (fs) | $\tau$ (fs) | PIT (fs) |
|-----------|-------------|---------|-------------|---------|-------------|---------|-------------|---------|
| 4d-Eout   | 258         | 556     | 182         | 570     | 119         | 618     | 203         | J(a)    |
| 2         | 316         | 538     | 189         | 569     | 268         | 526     | 220         | J(a)    |
| 3         | 304         | 535     | 156         | 454     | 227         | 182     | 452         | J(a)    |
| 4         | 308         | J(a)    | 178         | J(a)    | 262         | J(a)    | 209         | J(a)    |
| 5         | 151         | 584     | 158         | J(a)    | 228         | 524     | 187         | 497     |
| 6         | 259         | 687     | 156         | 380     | 209         | 555     | 192         | 620     |
| 7         | 224         | J(a)    | 176         | J(a)    | 239         | J(a)    | 179         | J(a)    |
| 8         | 203         | J(a)    | 170         | 625     | 293         | 530     | 162         | J(a)    |
| 9         | 209         | 575     | 184         | J(a)    | 253         | 544     | 167         | J(a)    |
| 10        | 312         | 508     | 159         | 625     | 245         | 477     | 167         | 596     |
| average   | 254         | 569     | 171         | 537     | 240         | 539     | 187         | 541     |

[a] Trajectory does not complete the photoisomerization within 700 fs. [b] Average value over all trajectories.

### 3. Conclusions

We have presented a minimal design of molecular motors that can be driven by visible light and are able to produce fast and
efficiency rotary motion without intermediary thermal steps. Specifically, with it proven difficult to realize all of these desirable features simultaneously in one and the same motor design, we have demonstrated computationally that a small Schiff-base motor (4d) comprising only five conjugated double bonds is successful in this regard. In particular, using state-of-the-art techniques based on multi-configurational quantum chemistry, it is found that this motor achieves a full 360° rotation from consecutive, visible-light-triggered (∼2.8 eV at the CASPT2 level) E/Z photoisomerizations alone, and that these processes are both fast (r ≈ 170–250 fs) and efficient. We hope that these results will stimulate further investigation of ways to exploit usefully the favorable features of synthetically realizable Schiff-base systems in the future development and application of molecular motors. In this regard, a brief retrosynthetic analysis for the actual preparation of 4d is presented in the Supporting Information (see Scheme S1).

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Conflict of Interest

The authors declare no conflict of interest.

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