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A Pentiptycene-Derived Molecular Brake: Photochemical $E \rightarrow Z$ and Electrochemical $Z \rightarrow E$ Switching of an Enone Module

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Abstract: The synthesis and brakelike performance of a new molecular system (1) consisting of a pentiptycene rotor and a 2-methyleneindanone brake are reported. The rotation kinetics of the rotor was probed by both variable-temperature ¹H and ¹³C NMR spectroscopy and DFT calculations, and the switching between the brakeon and brake-off states was conducted by a combination of photochemical and electrochemical isomerization. Because of the greater steric hindrance between the rotor and the brake units

Introduction

Artificial molecular machinery is an important subject in the areas of nanoscience and nanotechnology.^[1,2] A common feature for all prototypes of molecular machines is the presence of distinct mechanical states (dynamic or static) that can be switched or biased by external stimuli (energy input) such as light, electrical energy, chemicals, and heat. The machinelike movements associated with the switching processes perform the designated work, leading to so-called molecular

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in the Z form ((Z)-1) than in the E form ((E)-1), rotation of the rotor is slowed down 500-fold at room temperature (298 K) on going from (E)-1 to (Z)-1, corresponding to the brake-off and brake-on states, respectively. The $(E)-1\rightarrow(Z)-1$ photoisomerization in acetonitrile is efficient and reaches an (E)-1/(Z)-1 ratio of 11:89 in the photo-

Keywords: conformation analysis • electrochemistry • isomerization • molecular devices • photochemistry stationary state upon excitation at 290 nm, attributable to a much larger isomerization quantum efficiency for (E)-1 versus (Z)-1. An efficient (Z)-1 \rightarrow (E)-1 isomerization (96%) was also achieved by electrochemical treatment through the radical anionic intermediates. Consequently, the reversibility of the E-Z switching of 1 is as high as 85%. The repeated E-Z switching of 1 with alternating photochemical and electrochemical treatments is also demonstrated.

shuttles, motors, brakes, and many others.^[1–13] Undoubtedly, the state-to-state switching should be as selective and efficient as possible. In addition, light and electrical energy are cleaner energy sources than chemicals, because they are free of the problem of the accumulation of chemical waste during operation.^[2] A clean and highly efficient switching mode is in particular demand for operating molecular machines on a single-molecule level or in a nanosized domain.

The *cis/trans* (*Z*–*E*) photoisomerization is one of the most important switching modes in light-driven molecular machines.^[4–6] Because of the comparable photoactivity for the *E* and *Z* isomers in most cases, the switching direction and efficiency are determined mainly by their relative molar absorptivity at the excitation wavelengths. Ideally, each of the isomers can be selectively excited to reach a quantitative conversion. However, this is generally not the case due to the spectral overlap of the isomers, and therefore examples of high efficiency (e.g., >85%) for both the $E \rightarrow Z$ and $Z \rightarrow$ *E* photoisomerizations are rare.^[6]

Several redox centers have been employed for the construction of electrochemically driven molecular machines. Examples include Cu^{I}/Cu^{II} ,^[7] Ni^{II}/Ni^{III}/Ni^{IV},^[8] C_{60}/C_{60} ,^[9] tetrathiafulvalene (TTF)/TTF⁺⁺/TTF²⁺,^[10] methyl viologen

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(MV²⁺)/MV⁺⁺,^[11] naphthalimide/naphthalimide^{-,[12]} and ferrocene/ferrocene⁺.^[13] In these cases, the different redox states correspond to different mechanical states, and the machinelike movements are thermodynamically driven in response to a change in the redox states. To our knowledge, a molecular machine that employs electrochemical reactions as a switching mode between two neutral and non-redox-related mechanical states has yet to be demonstrated.

Herein we report a new approach toward the efficient control of molecular machines by a combination of directional photochemical $E \rightarrow Z$ and electrochemical $Z \rightarrow E$ isomerization, as demonstrated by the molecular brake system **1** (Scheme 1). The two stereoisomers (*E*)-**1** and (*Z*)-**1** corre-



Scheme 1. Synthesis of the *E* and *Z* isomers of **1** and **2**. The numerical labels for protons and carbons are for discussion of the VT NMR spectra. The symbol φ denotes the dihedral angle between the two phenylene planes.

spond to the brake-off and brake-on mechanical states, respectively. The E-Z switching results in a 500-fold change in the Brownian rotation rate of the pentiptycene group (the rotor) at room temperature due to the different extent of steric interaction with the indanone unit (the brake component) in the two stereoisomers: the smaller steric demand of the methylene versus the carbonyl groups in the indanone moiety leads to a lower barrier for the rotation of the rotor in (E)-1 than in (Z)-1. In conjunction with the behavior of model compounds (E)-2 and (Z)-2 (Scheme 1), it is shown that the pentiptycene group in 1 plays a critical role in both the photochemical and electrochemical switching processes.

Results and Discussion

Synthesis: The synthesis of **1** and **2** is outlined in Scheme 1. Compounds (E)-**1** and (E)-**2** are prepared through crossed aldol condensation reactions between 1-indanone and the corresponding benzaldehydes **3** and **4**. The synthesis of the pentiptycene carboxaldehyde **3** has been reported previously,^[14] and the benzaldehyde **4** is commercially available.

Whereas (*E*)-**2** was obtained in a good yield (86%) by heating the two carbonyl components in acidic ethanol solutions,^[15] the synthesis of (*E*)-**1** was base-promoted and required the assistance of microwave irradiation and the KF/ Al_2O_3 catalyst^[16,17] to reach a high yield (82%). For comparison, the yield for (*E*)-**1** drops to 37% with the same reagents when heated for 16 h. The corresponding *Z* isomers can be obtained through photoisomerization of the *E* isomers in solutions. For the purposes of good solubility, THF was adopted as the solvent. A 352 nm light source was employed. This wavelength corresponds to the onset of the absorption profile of (*E*)-**1** in THF (Figure S1, Supporting Information), so that deep penetration of the light to the opti-

> cally dense solutions (1-1.5 mM)is allowed. Although the wavelength of 352 nm is near the absorption maximum of (E)-**2** (Figure S2), it gave a larger (Z)-**2**/(E)-**2** ratio in the photostationary state (PSS) than the light of longer wavelength (vide infra). It should also be noted that the use of shorter wavelength light led to a lower yield due to the formation of unidentified by-products.

> **DFT calculations**: The thermochemistry of (E)-1 and (Z)-1 was evaluated by DFT calculations at the BMK/6-311+G**// B3LYP/6-31G* level. We have shown previously^[5] that this level of theory reproduces the experimental results of pentip-

tycene-based molecular brakes quite well. To expedite the calculations, the octyloxy group on the pentiptycene rotor was replaced by a methoxy group. Each isomer of (E)-1 and (Z)-1 was found to have two optimized ground-state conformers, which differ merely in the syn or anti orientation of the two groups, methoxy and 2-methyleneindanone, with respect to the central phenylene ring of the pentiptycene rotor. The difference in energy between the two conformers in each case is less than 0.7 kcalmol⁻¹ (Table S1 in the Supporting Information). Thus, the reported free energy at 298 K is estimated on the basis of the free energies of the two conformers with consideration of the Boltzmann distribution, rather than the lowest energy structures of the ground and transition states. The results suggest that (E)-1 is more stable than (Z)-1 by 5.86 kcalmol⁻¹ free energy. This is consistent with the fact that (Z)-1 was not observed in the products of the aldol condensation reaction. The conjugation effect appears to be unimportant in accounting for their relative stability, because in the lowest-energy groundstate structures (Figure 1), the dihedral angle (ϕ , defined in Scheme 1) between the two phenylene rings along the long molecular axis is larger in (E)-1 (\approx 80°) than in (Z)-1

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Figure 1. DFT-derived lowest-energy ground-state (GS) and transitionstate (TS) structures for the rotation about the aryl–vinyl C–C bond in a) (E)-1 and b) (Z)-1. The units of labeled distances and angles are Å and degrees, respectively.

($\approx 60^{\circ}$). In fact, if ϕ were set to 60° for (*E*)-1, one of the methylene H atoms of the indanone moiety would have extremely close contact with a nearby H atom of pentiptycene (<1.9 Å). A coplanar π -conjugated backbone (i.e., $\phi = 0^{\circ}$) in 1 would also encounter severe steric congestion between the pentiptycene bridgehead nuclei and the methylene ((*E*)-1) or the carbonyl groups ((*Z*)-1) of the indanone, and these conformations correspond to the transition states of rotation about the aryl–vinyl C–C bond (Figure 1). The calculated free-energy rotational barriers at 298 K (ΔG^{+}_{298}) are 11.86 and 14.38 kcal mol⁻¹ for (*E*)-1 and (*Z*)-1, respectively, which predicts a 10^{2} -fold difference in rotation rate ($\Delta \Delta G^{+}_{298} = 2.52$ kcal mol⁻¹).

For comparison, the model compounds (E)-2 and (Z)-2 were also studied. Unlike 1, the ground states of (E)-2 and (Z)-2 adopt a coplanar geometry and the rotational transition states exhibit a perpendicular orientation of the two phenylene rings (Figure S3 in the Supporting Information). The argument of a twisted versus planar π -conjugated backbone in 1 versus 2 is indeed supported by the significantly blue-shifted UV/Vis absorption spectra (vide infra). The *E* isomer remains more stable than the *Z* isomer in 2, but the free-energy difference becomes smaller (3.59 kcalmol⁻¹) compared to that of 1. In addition, the rotational barriers for (E)-2 and (Z)-2 are similar (4.80 and 5.03 kcalmol⁻¹, respectively), and are much lower than those for 1. Evidently, the steric effect imposed by the bulky pentiptycene group plays an important role in the relative energies of the conformers of **1**.

Variable-temperature NMR experiments: The rotational barriers and activation parameters of (E)-1 and (Z)-1 were also evaluated by variable-temperature (VT) NMR spectroscopy. Figure 2 shows the pentiptycene peripheral phenylene region of the ¹H and ¹³C NMR spectra of (*E*)-1 and (*Z*)-1 in CD₂Cl₂ at 253 K. The signals can be assigned unambiguously on the basis of a series of 2D NMR experiments, including COSY, HSQC, NOESY, and ROESY (Figures S5-S12 in the Supporting Information). The presence of two sets of signals (Figures 2a and 2b) for (Z)-1 but not for (E)-1 confirms that the former possesses a larger rotational barrier than the latter. Nevertheless, we observed decoalescence of the signals (e.g., H1 and C6) in both the ¹H and ¹³C NMR spectra for (E)-1 upon cooling to a temperature near 213 K. In the case of (Z)-1, rotation of the rotor is already arrested on the NMR timescale at 253 K. Thus, the temperature was raised to reach coalescence of the signals (e.g., nuclei H4 and C3 at 293 K). Line shape analyses of both the ¹H and ¹³C VT NMR spectra (Figures 2c and 2d) provide the rotation rate constants (k), and thus the activation barriers (E_a) , and the enthalpy (ΔH^{\dagger}) and entropy (ΔS^{\dagger}) of activation through Arrhenius and Eyring plots (Figures S13-S17 in the Supporting Information). These data, along with the free energy of activation at 298 K, are summarized in Table 1. The observed difference in ΔG^{\dagger}_{298} (3.8 kcalmol⁻¹) between (*E*)-1 and (*Z*)-1 is of the same order of magnitude as that predicted by DFT calculations (vide supra), and suggests a 500-fold difference in the rotation rate at 298 K. Because of the similar ΔS^{\dagger} values for (E)-1 and (Z)-1, their difference in ΔG^{\dagger}_{298} mainly results from the enthalpic term. This is consistent with the rigidity of the brake component, which lacks internal rotational freedoms.

Photochemical (E)-1 \rightarrow (Z)-1 switching: With the different rotation rates for the rotor in (E)-1 (fast rotation) and (Z)-1 (slow rotation), compound 1 behaves as a molecular brake in which the carbonyl group serves as the brake latch (Figure 3). To switch between the brake-off and brake-on states, we have to conduct E-Z isomerization reactions. This was carried out in acetonitrile (0.5 mM), as a quick comparison between CH₂Cl₂, THF, and acetonitrile showed that the latter is superior in the switching efficiency for both the photochemical (E)-1 \rightarrow (Z)-1 and the reverse electrochemical (Z)-1 \rightarrow (E)-1 switching. The details are described in the following.

Due to the nearly overlapped absorption spectra for (E)-1 and (Z)-1 (Figure 4), the selective excitation of either (E)-1 or (Z)-1 is essentially impossible. However, to our surprise, the photochemical (E)-1 \rightarrow (Z)-1 switching in acetonitrile with excitation at 290 nm is as high as 89% in PSS according to HPLC analysis (Figure 5 a).^[18] This must indicate that the isomerization quantum yield for (E)-1 \rightarrow (Z)-1 (Φ_{EZ}) is much larger than that for (Z)-1 \rightarrow (E)-1 (Φ_{ZE}) according to Equation (1), for which the molar ratio of (Z)-1/(E)-1 in PSS

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Figure 2. Pentiptycene peripheral phenylene (blade of the rotor) region of the a) ¹H NMR and b) ¹³C NMR spectra of (*E*)-1 and (*Z*)-1 in CD₂Cl₂ at 253 K. c) VT ¹H NMR and d) VT ¹³C NMR spectra of (*E*)-1 (H₁ and C₆) and (*Z*)-1 (H₄, C₂, and C₃) in CD₂Cl₂, for experimental data (left) and simulated data (right). Values of temperature (T, K) and interconversion rate (k, s⁻¹) between the two isoenergetic states are also given for each trace. See Scheme 1 for nuclei labeling and Figure S4 in the Supporting Information for more complete VT ¹H NMR spectra for (*E*)-1.

Table 1. VT ¹H NMR and ¹³C NMR data and activation parameters for the rotation of the pentiptycene rotor in (*E*)-1 and (*Z*)-1.^[a]

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	Nuclei ^[b]	$T_c^{[c]}$ [K]	$\Delta {G^{*}}_{ ext{c}}$ [kcal mol $^{-1}$]	E_a [kcal mol ⁻¹]	$\log A$	ΔH^{*} [kcal mol ⁻¹]	ΔS^{\pm} [cal mol ⁻¹ K ⁻¹]	$\Delta G^{*}_{_{(298\mathrm{K})}}$ [kcal mol ⁻¹]	$k_{(298\mathrm{K})} \ [\mathrm{s}^{-1}]$	
(E)- 1	H (1,1') ^[d]	213	10.2	8.3 ± 0.1	10.6 ± 0.1	7.8 ± 0.1	-12.0 ± 0.6	11.4 ± 0.2	20567	
	C (6,6') ^[e]	203	10.4	8.3 ± 0.3	10.7 ± 0.3	7.9 ± 0.3	-11.0 ± 1.2	11.1 ± 0.4	_	
(Z)- 1	$H (4,4')^{[f]}$	293	15.0	12.6 ± 0.5	11.0 ± 0.4	12.1 ± 0.5	-10.1 ± 1.8	15.1 ± 0.8	37	
	C (2,2'; 3,3') ^[f]	283, 293	15.0,15.5	11.4 ± 0.7	10.2 ± 0.6	10.8 ± 0.7	-13.9 ± 2.6	15.0 ± 1.1	42	

[a] Recorded in CD₂Cl₂. [b] For line shape analysis. See Scheme 1 for the nuclei labels. [c] Coalescence temperature. [d] Temperature range 193–293 K, 11 data points. [e] Temperature range 183-243 K, seven data points. [f] Temperature range 263-293 K, four data points.



Figure 3. Schematic representation of the brake function of 1.

 $([(Z)-1]/[(E)-1]_{PSS})$ is determined not only by the relative molar absorptivity of (E)-1 ($\varepsilon_{\rm E}$) and (Z)-1 ($\varepsilon_{\rm Z}$) at the excitation wavelengths (λ_{ex}) but also by the relative values of Φ_{EZ} and Φ_{ZE} .

$$[(Z)-\mathbf{1}]/[(E)-\mathbf{1}]_{PSS} = (\varepsilon_E \Phi_{EZ})/(\varepsilon_Z \Phi_{ZE})$$
(1)

On the basis of $\varepsilon_E/\varepsilon_Z = 1.07$ and $[(Z)-1]/[(E)-1]_{PSS} = 8.09$ at $\lambda_{ex} = 290$ nm (Figure 4), a Φ_{EZ}/Φ_{ZE} ratio of 7.56 is predicted. This is indeed borne out by the observed quantum yields of $\Phi_{EZ}{=}0.53$ and $\Phi_{ZE}{=}0.08$.^[19] Such a large ratio of $\Phi_{EZ}{=}0.08$. observed for 1 is approaching so-called one-way photoisomerization. A few examples of one-way photoisomerization for alkenes, either $E \rightarrow Z$ or $Z \rightarrow E$, have been reported.^[10-22] The origins of the small or negligible isomerization quantum efficiency for one of the isomers could be either kinetic (i.e.,



Figure 4. UV/Vis absorption spectra for (*E*)-1, (*Z*)-1, (*E*)-2, and (*Z*)-2 in acetonitrile.



Figure 5. HPLC chromatograms of a) (*E*)-1 before (trace I) and after (trace II) irradiation with 290 nm light, b) (*Z*)-1 before (trace III) and after (trace IV) electrochemical treatment (see text for details), and c) (*E*)-1 (trace 0) after alternating 290 nm irradiation (odd-numbered traces) and electrochemical treatment (even-numbered traces). The system is operated in acetonitrile solution.

a high torsional barrier or the presence of ultrafast deactivation routes)^[17] or thermodynamic (i.e., unfavorable equilibrium to the twisted excited state).^[21] In view of the fact that mutual (E)-2 \rightarrow (Z)-2 and (Z)-2 \rightarrow (E)-2 photoisometization reactions occur with quantum yields of 0.50 and 0.23, respectively,^[23] we can conclude that the inefficient (Z)-1 \rightarrow (E)-1 photoisomerization is associated with the bulky pentiptycene group. A tentative explanation for the distinct Φ_{EZ} and Φ_{ZE} values is based on the different dihedral angles ϕ between the pentiptycene central ring and the 2-methyleneindanone group (Scheme 1). The large ϕ value (80°) in (E)-1 might lead to an excited state more localized in the 2-methyleneindanone group (the red part in Figure 3), and thus direct rotation about the C=C bond is feasible. Excitation of (Z)-1 might lead to a planarization relaxation of the π -conjugated benzylideneindanone backbone due to a smaller ϕ (60°), but this process would encounter severe steric congestion between the bridgehead hydrogen atoms and the car-

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bonyl group, a scenario similar to the transition state for the aryl-vinyl rotation of (Z)-1 (Figure 1b). The subsequent C= C torsion would also result in a sterically hindered state resembling the transition structure for the aryl-vinyl rotation of (E)-1. These steric interactions could abort the isomerization, causing a low Φ_{ZE} value.

Electrochemical (Z)-1 \rightarrow (*E*)-1 switching: The advantage of a low Φ_{ZE} value in the photochemical (E)-1 \rightarrow (Z)-1 switching precludes the use of light as an efficient switching method for the reverse process, (Z)-1 \rightarrow (E)-1. An alternative isomerization pathway is thus required. We proposed that this might be achieved electrochemically, because it is known that many radical ions of diarylethenes undergo the $Z \rightarrow E$ isomerization efficiently.^[24] This phenomenon can be understood by considering a reduced double-bond character for the vinyl group in the radical ionic states, as is the case in the electronically excited state for photoisomerization; thus, the equilibrium of the isomers is driven toward the more stable E isomer. Because of the electron-accepting enone group in 1, the proposed redox-induced (Z)- $1 \rightarrow (E)$ -1 isomerization could proceed via the radical anions, as shown in Equation (2).

$$(Z)-\mathbf{1} + e^{-} \to [(Z)-\mathbf{1}]^{\bullet-} \longrightarrow [(E)-\mathbf{1}]^{\bullet-} \to (E)-\mathbf{1} + e^{-}$$
(2)

This rationale is indeed promising in view of the reversible cathodic waves and the similar values of reduction potential ($E_{\rm red} = -1.52$ and -1.49 V vs. SCE for (*E*)-1 and (*Z*)-1, respectively) in the cyclic voltammograms (CVs) (Figure 6a) of (*E*)-1 and (*Z*)-1. This indicates that both the intermediates [(*E*)-1]⁻⁻ and [(*Z*)-1]⁻⁻ are sufficiently stable under the experimental conditions, and have a relative stability similar to that in their neutral forms, which is ≈ 5 kcal mol⁻¹ more stable for (*E*)-1 than (*Z*)-1 based on DFT calculations (vide supra). Consequently, the equilibrium of the radical anions should be driven toward the *E* isomer, as shown in Equation (2).



Figure 6. CV curves of a) (*E*)-1 and (*Z*)-1 and b) (*E*)-2 and (*Z*)-2 in acetonitrile (0.3 mM, 0.1 M tetrabutyl ammonium tetrafluoroborate) recorded at 100 mV s⁻¹.

The electrochemical (Z)-1 \rightarrow (E)-1 switching experiment was conducted in N₂-bubbled anhydrous acetonitrile containing 0.5 mm (Z)-1 and 0.1 m Bu₄NPF₆ electrolyte, in a 1 mm quartz cell equipped with a platinum grid, a platinum

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wire, and a silver metal wire as the working, counter, and reference electrodes, respectively. To minimize possible intermolecular side reactions (e.g., dimerization) of the intermediates $[(Z)-1]^{--}$ and $[(E)-1]^{--}$, we employed potential pulses to keep a low concentration and short duration of the intermediates in solution. The voltage was switched between 0 and -1.55 V (the reduction peak potential vs. SCE), with 10 s and 20 s dwell time for the reduction and oxidation processes, respectively (Figure 7a). An (E)-1/(Z)-1 ratio of 96:4 was achieved with around 11 pulses (Figure 5b).



Figure 7. Potential programs for redox-induced a) (Z)-1 \rightarrow (E)-1 and b) (Z)-2 \rightarrow (E)-2 isomerization in acetonitrile. Two potential pulses are depicted for each case.

We believe that steric shielding of the enone redox center by the bulky pentiptycene group plays an important role in the stability of the radical anion intermediates. Indeed, this is confirmed by comparison with the model compound 2. The cathodic CV curve for (Z)-2 is irreversible (Figure 6b), and unidentified by-products quickly built up when (Z)-2 was subjected to the same electrochemical treatments as (Z)-1. Nevertheless, a new potential program (Figure 7b) with intermittent cyclic voltammetric scans between 0 and -1.45 V for (Z)-2 was able to overcome this problem and allow a 95% conversion of (Z)-2 \rightarrow (E)-2 (\approx 8 scans). The fact that (E)-1 and (E)-2 can also be reduced under the applied potentials (Figure 6) but survive in the final stage of electrochemical treatments supports the conclusion that the equilibrium in the radical anions favors the E isomer [Eq. (2)].

These results (an 89% (E)-1 \rightarrow (Z)-1 and a 96% (Z)-1 \rightarrow (E)-1 isomerization) account for the overall efficiency of 85% for the operation of the molecular brake (see Supporting Information for a motion picture for this concept). Figure 5c shows five cycles of an alternating forward photoisomerization and backward electrochemical isomerization of (E)-1 in acetonitrile. The small amount of fatigue (<5%) of the system demonstrates that electrochemical E-Z isomerization is a potential method for operating molecular machines.

Conclusion

We have demonstrated the first example of combined lightdriven $E \rightarrow Z$ and electrically driven $Z \rightarrow E$ isomerization to achieve a high switching efficiency in the operation of a molecular brake. Efficient control of the mechanical states of artificial molecular machinery using light and/or electrical energy has the advantages of clean energy input, time and power economy, and maximum work performance. These merits are particularly critical for constructing nanosized molecular machinery or integrated molecular devices.

Experimental Section

Methods: NMR spectra were acquired on a Bruker DMX 500 or Bruker AVIII 400 spectrometer using 5 mm gradient TBI and TBO probes, respectively. The chemical shifts for ¹H and ¹³C NMR spectra were referenced to the signals of tetramethylsilane $(\delta({}^{1}H)=0 \text{ and } \delta({}^{13}C)=0)$. Single-pulse spectra were recorded using a 30° pulse and a suitable delay time (2 s and 6 s for ¹H and ¹³C respectively). Other spectra (COSY, NOESY, ROESY, and HSQC) were measured using pulse sequences in the Bruker software package. In the case of variable-temperature measurements, the actual sample temperature was well calibrated by ¹H signals of ethylene glycol and methanol, so that the temperature error was within ± 1 K. Signal acquisition was begun after a sufficient temperature equilibration time (10–15 min). The fitting of dynamic NMR line shapes at different temperatures was performed with the Topspin 2.0 program, Bruker BioSpin Group. Infrared spectra were recorded on a Varian 640-IR FTIR spectrometer. UV/Vis absorption spectra were measured on a Varian Cary300 Bio-type at room temperature. Quantum yields of photoisomerization were measured on optically dense N2-bubbled solutions $(10^{-3} M)$ at 313 nm using a 75 W Xe arc lamp and monochromator. trans-4-(Phenylamino)stilbene was used as a reference standard ($\Phi_{tc} = 0.34$ in dichloromethane).^[19] Photoisomerization quantum yield measurements were conducted in N₂-bubbled THF/acetonitrile (v/v = 1/4) solutions (0.5 mm) at selected wavelengths using a 75 W Xe arc lamp and monochromator. The extent of photoisomerization (<10%) was determined using HPLC analysis (Waters 600 Controller and 996 photodiode array detector) without back-reaction corrections. The reproducibility error was <10% of the average. The cyclic voltammetry (CV) data were recorded on a CHI612B electrochemical analyzer at room temperature (23±1°C), and a glassy carbon electrode served as the working electrode. The substrates were 0.3 mm in acetonitrile containing 0.1 m Bu₄NPF₆ as supporting electrolyte. The potentials were calibrated against SCE by the addition of ferrocene (Fc) as an internal standard, taking E^0 -(Fc/Fc⁺)=0.52 V versus SCE in CH₂Cl₂. The electrochemical reduction experiments were carried out in a 1 mm quartz cell with N2-bubbled MeCN solutions containing 0.5 mm substrate and 0.1 m Bu₄NPF₆ as electrolyte. A Pt grid was used as the working electrode, a Pt wire as the counter electrode, and an Ag wire as the reference electrode. The extent of electrochemical isomerization was also based on HPLC analysis. The DFT calculations were performed with the Gaussian03 program.^[25] Freeenergy values were estimated by combining the single-point energies at the BMK/6-311+G** level and the thermal corrections for Gibbs free energy calculated from frequency analyses at the B3LYP/6-31G* level^[26] in the gas phase with the consideration of the Boltzmann distribution of the possible conformations of the substituents.

Materials: Anhydrous THF and MeCN were obtained from the solvent purifier SPBT-103 of LC Technology Solutions Inc., equipped with an SP-505 column. The moisture content was less than 10 ppm. All the other solvents and materials for synthesis were reagent grade. Detailed synthetic procedures and structural characterization data for compounds **1** and **2** are provided below.

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Compound (E)-1: Supported KF catalysts (10 wt%) were prepared by impregnation of supports (neutral Al₂O₃, 9 g) to incipient wetness with solutions of KF (1 g) in methanol (2 mL)/water (2 mL). The slurry was stirred for 2 h and then the solvent was evaporated on a rotary vacuum evaporator. Afterwards, the catalyst was dried at 150°C for 24 h, and then stored in a desiccator.^[16] A mixture of aldehyde 3 (0.080 g, 0.14 mmol) and indanone (0.016 g, 0.15 mmol), sodium acetate (0.024 g, 0.30 mmol), supported KF catalysts (1.0 g of 10 wt %; also containing 0.14 mmol of KF), and CH₂Cl₂ (20 mL) was stirred for 30 min. The solution was concentrated under reduced pressure, and then the solvent was evaporated off under vacuum to obtain a powdered dry solid. The reactants adsorbed onto the solid surface. The solid was mixed with acetic anhydride (5 mL) in a round-bottomed flask, and the mixture was irradiated in a microwave oven at 550 W for 15 min. After cooling, the reaction mixture was dissolved in CH2Cl2 and H2O. The organic layer was washed with H₂O and then dried over anhydrous MgSO₄, and the filtrate was concentrated under reduced pressure. Column chromatography with CH_2Cl_2 /hexane (1:2) as eluent afforded (E)-1 as a pure pale yellow solid. Yield: 82%; m.p. 197–199°C; ¹H NMR (500 MHz, CD_2Cl_2): $\delta = 0.97$ (t, J=7.0 Hz, 3H), 1.40-1.42 (m, 4H), 1.46-1.58 (m, 4H), 1.73 (quint, J= 7.6 Hz, 2H), 2.07 (quint, J=7.6 Hz, 2H), 3.32 (s, 2H), 4.00 (t, J=6.8 Hz, 2H), 5.38 (s, 2H), 5.76 (s, 2H), 6.90-6.97 (m, 8H), 7.21 (d, J=7.0 Hz, 4H), 7.36 (d, J=7.0 Hz, 4H), 7.39 (d, J=7.6 Hz,1 H), 7.53 (t, J=7.3 Hz, 8H), 7.66 (t, J=7.3 Hz, 1H), 8.02 (s, 1H), 8.04 ppm (s, 1H); ¹³C NMR $(125 \text{ MHz}, \text{CD}_2\text{Cl}_2): \delta = 14.4, 14.5, 23.2, 23.3, 27.0, 29.0, 30.2, 30.3, 31.2,$ 31.6, 32.2, 32.5, 48.7, 51.9, 76.8, 124.0, 124.2, 124.9, 125.7, 125.8, 127.1, 128.4, 131.5, 135.6, 136.0, 139.2, 142.4, 142.5, 145.7, 145.9, 150.0, 150.3, 193.4 ppm; IR (KBr): $\tilde{\nu} = 3068$, 3021, 1721, 1650, 1460, 742 cm⁻¹; FAB-HRMS: calcd for C₅₂H₄₄O₂: 700.3341; found: 700.3346.

Compound (Z)-1: A N₂-bubbled solution of (E)-1 (0.015 g, 0.02 mmol) in THF (20 mL) was irradiated with a photochemical reactor at 352 nm for 1 h. The solvent was removed under reduced pressure, and the resulting solid was purified by preparative HPLC with EA/hexane (1:1.5) as eluent to afford the pure vellow solid of (Z)-1. Yield: 81%: m.p. 296–298°C: ¹H NMR (500 MHz, CD₂Cl₂): $\delta = 0.84-0.90$ (m, 3 H), 0.95-0.98 (m, 2 H), 1.40-1.48 (m, 4H), 1.49-1.58 (m, 2H), 1.73 (quint, J=7.6 Hz, 2H), 2.08 (t, J=7.3 Hz, 2H), 4.00 (t, J=6.3 Hz, 2H), 4.26 (s, 2H), 5.37 (s, 1H), 5.72 (s, 1H), 6.88-6.95 (d, 8H), 7.08 (s, 2H), 7.21-7.33 (m, 7H), 7.51-7.50 (m, 1 H), 7.72–7.74 (m, 2 H), 7.79 ppm (d, J = 7.5 Hz, 1 H); ¹³C NMR (125 MHz, CD_2Cl_2): $\delta = 14.5$, 23.3, 27.0, 30.0, 30.2, 31.1, 32.5, 34.1, 48.6, 48.7, 49.1, 52.0, 76.8, 123.8, 124.0, 124.3, 124.4, 124.6, 125.4 125.6, 125.7, 125.8, 127.0, 128.2, 132.2, 135.1, 135.2, 139.1, 140.4, 142.9, 145.3, 145.6, 149.8, 150.0, 191.7 ppm; IR (KBr): $\tilde{\nu}$ =3065, 3017, 1702, 1637, 1459, 740 cm⁻¹; HRMS (ESI⁺): m/z: calcd for C₅₂H₄₄O₂Na⁺: 723.3241 [*M*⁺+Na]; found: 723.3241.

Compound (E)-2: A mixture of 1-indanone (0.7 g, 6.5 mmol), aldehyde **4** (1.5 g, 6.4 mmol), HCl (0.1 mL, 37 wt %), and EtOH (25 mL) was heated at 80 °C for a period of 18 h. The reaction mixture was cooled to RT to give a yellow solid. The solid was filtered, washed with EtOH, and recrystallized in hexane/dichloromethane to provide 1.82 g of (*E*)-**2**. Yield: 86%; m.p. 88–90 °C; ¹H NMR (400 MHz, CDCl₃): δ =0.88–0.91 (m, 3 H), 1.29–1.35 (m, 8H), 1.43–1.48 (m, 2H), 1.80 (quint, *J*=6.7 Hz, 2H), 3.98–4.01 (m, 2H), 6.95–6.97 (m, 2H), 7.40 (t, *J*=7.6 Hz, 2H), 7.53–7.64 (m, 5H), 7.89 ppm (d, *J*=7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ =14.1, 22.6, 26.0, 29.1, 29.2, 29.3, 31.8, 32.4, 68.1, 114.9, 124.2, 126.0, 127.5, 127.9, 132.2, 132.5, 133.9, 134.2, 138.2, 149.4, 160.5, 194.3 ppm; IR (KBr): $\bar{\nu}$ = 3372, 1690, 1598, 1250, 1178, 732 cm⁻¹; HRMS (ESI⁺): *m/z*: calcd for C₅₂H₄₄O₂H⁺: 349.2168 [*M*⁺+H]; found: 349.2147.

Compound (Z)-2: A N₂-bubbled solution of (*E*)-**2** (10 mg, 0.03 mmol) in THF (20 mL) was irradiated with a photochemical reactor at 352 nm for 1 h. The solvent was removed under reduced pressure, and the resulting solid was purified by flash chromatography with EtOAc/hexane (1:6) as eluent to afford the pure pale yellow solid of (*Z*)-**2**. Yield: 69%; m.p. 81–82 °C; ¹H NMR (400 MHz, CDCl₃): δ =0.88–0.92 (m, 3H), 1.30–1.35 (m, 8H), 1.43–1.49 (m, 2H), 1.80 (quint, *J*=7.6 Hz, 2H), 2.05 (quint, *J*=6.7 Hz, 2H), 3.87 (s, 2H), 4.01 (t, *J*=6.6 Hz, 2H), 6.91–6.93 (m, 3H), 7.38–7.42 (m, 1H), 7.46–7.48 (m, 1H), 7.55–7.59 (m, 1H), 7.85 (d, *J*=7.6 Hz, 1H), 8.18–8.20 ppm (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ =

14.1, 22.6, 26.0, 29.1, 29.2, 29.3, 31.8, 35.4, 68.0, 114.0, 124.1, 125.7, 127.3, 127.6, 132.3, 133.3, 133.9, 139.5, 140.8, 148.6, 160.6, 192.0 ppm; IR (KBr): $\bar{\nu}$ =1677, 1594, 1182, 972, 737 cm⁻¹; HRMS (ESI⁺): *m/z*: calcd for C₅₂H₄₄O₂H⁺: 349.2168 [*M*⁺+H]; found: 349.2151.

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