# Illuminating Photoswitchable Catalysis

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ABSTRACT: Through the realization of conceptually new approaches aimed at controlling chemical reactions using light, the field of photoswitchable catalysis has seen rapid development over the past three decades. Although many photoswitchable catalysts are heterogeneous and utilize photosensitive surfaces, such as TiO_2 and CdSe, significant attention has also been directed toward homogeneous analogues, primarily by capitalizing on the steric changes that accompany the $E \rightarrow Z$ photoisomerizations of azobenzene or stilbene derivatives. More recently, photochromic diarylethene moieties have been used to switch the intrinsic catalytic activities and selectivities through alteration of the steric and electronic properties displayed by a supporting ligand. In addition to detailing the aforementioned advances, this perspective summarizes other important developments in photoswitchable catalysis and offers a viewpoint on the future outlook of the field.

KEYWORDS: catalyst, photoswitchable, photochromism, azobenzene, diarylethene
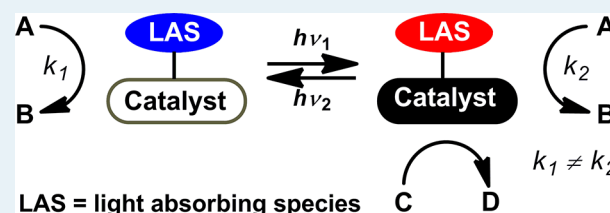
INTRODUCTION

Many of the essential functions found in living organisms are controlled by molecular units that undergo changes triggered by external stimuli. Indeed, many biological systems harness externally applied energy and use it to regulate molecular transport or catalytic phenomena with exquisite spatial and temporal control. In contrast, synthetic chemical processes are typically limited to a fixed rate and/or selectivity once the reaction conditions are chosen. Incorporating stimuli-responsive units into synthetic processes may enable switchable catalytic activities and/or selectivities, and facilitate applications that range from streamlined multistep syntheses to the production of polymers with sophisticated microstructures.[1]

Significant efforts in the field of catalysis have been directed toward the optimization of catalyst structure to achieve high substrate conversions and/or high regio-, chemo-, or stereo-selectivities. More recently, however, efforts have focused on using external stimuli, including acid–base chemistry,[2] mechanical force,[3] redox processes,[4] and light[5] to modulate the intrinsic activities and/or selectivities displayed by catalysts. Light, in particular, is an attractive stimulus as it is noninvasive, offers excellent temporal and spatial resolution, and can be precisely controlled with an appropriate source. Furthermore, using light of predetermined wavelengths allows for selective excitation and subsequent reactivity of specific molecular units in a highly controlled manner.

Photoresponsive processes found in nature, including photosynthesis and vision, illustrate the power of using electromagnetic radiation to initiate and regulate complex molecular and biochemical processes, and underscore the potential utility of synthetic catalysts that respond to light with similar precision. A number of conceptually different approaches have been used to realize artificial photoresponsive systems, including photocatalysis, photoactivated catalysis, and photoswi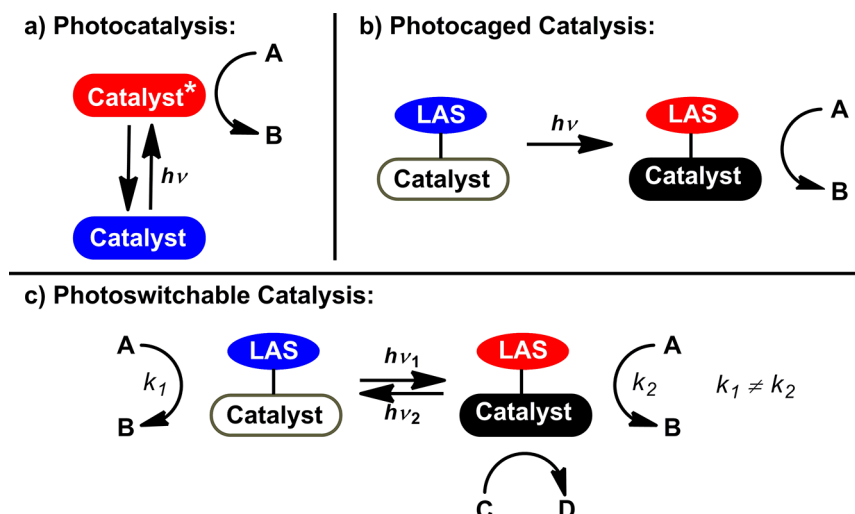tchable catalysis. In photocatalysis,[6] an inactive precatalyst is irradiated to generate a catalytically active, photoexcited state which subsequently reacts with a substrate (Figure 1a). In contrast, photoactivated or "photocaged" catalysis starts with an inactive catalyst species that, upon irradiation, becomes catalytically active (Figure 1b). Notable examples of photoactivated catalysis include photoacid and photobase generators,[7] as well as metal complexes that become activated upon the dissociation of photolabile ligands.[8,9] Photoswitchable catalysis involves a catalytically active species that undergoes a reversible photochemical transformation and, as a result, alters its intrinsic catalytic properties (Figure 1c). The catalyst in its initial state may be active or inactive, and the photoinduced transformation may either change the rate at which the catalyst facilitates a given reaction (A → B; $k_1 \neq k_2$) or may allow the catalyst to promote a different reaction (C → D). If the forward and reverse transformations are induced by orthogonal stimuli (i.e., different wavelengths of light), the catalyst may be toggled between two states that display different reactivities or selectivities via a remote light stimulus. Although more difficult to realize, photoswitchable catalysis offers distinct advantages over photocatalysis or photoactivated catalysis, since it adds the potential for controlling the catalyst as the reaction proceeds in addition to regulating the initiation process.

An ideal photoswitchable catalyst requires that the photo-induced transformation (i) occurs with high efficiency in both the forward and the reverse directions, (ii) causes a significant alteration in steric or electronic properties of the catalyst, and (iii) ultimately results in changes in catalytic activities and/or selectivities. Additionally, the photosensitive unit should be capable of absorbing light at a wavelength that will not excite

Figure 1. Representation of various approaches to light-mediated catalysis: (a) Photocatalysis involves the promotion of an inactive precatalyst to its active, photoexcited state. (b) In photoactivated catalysis, an inactive catalyst species undergoes a photochemical transformation to an active species. (c) Photoswitchable catalysis involves a reversible photochemical transformation that alters the intrinsic activity and/or selectivity displayed by a given photosensitive catalyst. LAS = light absorbing species.

other components of the same molecule or potential substrates to avoid premature photodegradation. A number of unique approaches that meet these requirements have been reported and are discussed herein.

This perspective aims to highlight the recent advances in the growing field of photoswitchable catalysis, including both heterogeneous and homogeneous systems. Heterogeneous photoswitchable catalysts have been achieved by employing catalytically active materials that undergo significant changes in their surface properties upon exposure to light. The development of homogeneous photoswitchable catalysis has primarily involved the incorporation of photochromic[10] functionalities, which may be reversibly switched between two states possessing different steric and/or electronic properties, into catalytically active species (Figure 2). For example, azobenzene[11] and stilbene[12] moieties, which undergo reversible photochemically driven $E \rightarrow Z$ isomerizations, have enabled the switching of catalytic activity through changes in sterics.
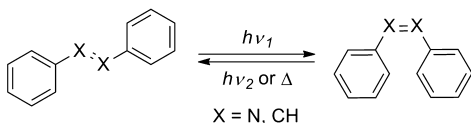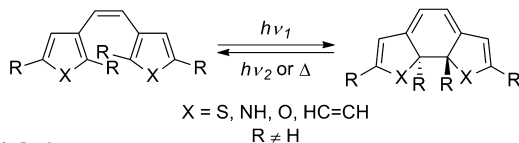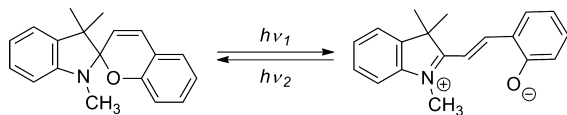


Figure 2. Photochromic units, including (a) azobenzene (X = N) or stilbene (X = CH), (b) diarylethenes, and (c) spiropyrans, commonly incorporated into photoswitchable catalyst scaffolds.

Diarylethenes,[13,14] which undergo an electrocyclic ring-closing reaction in the presence of light, have also been utilized for switching of both the steric and the electronic properties of catalysts. Similarly, the photoinduced changes in charge distribution that result from the ring-opening isomerization of spiropyrans[15] may also be used to alter catalytic activity.

## HETEROGENEOUS PHOTOSWITCHABLE CATALYSTS

Over the past 30 years, a variety of heterogeneous photoswitchable catalysts have been developed using the inherent photoresponsive properties of various surfaces or by attaching photoswitchable moieties to a material's surface. In an early example, the enzymatic activities displayed by peroxidases were photomodulated using cadmium selenide (CdSe) quantum dots (QDs), which are known to facilitate the formation of reactive oxygen species upon UV irradiation in aqueous media.[16] The heme-containing peroxidases, horseradish peroxidase, cytochrome C peroxidase, myoglobin, and CYP152A1, were all inactive in the presence of CdSe QDs in the dark, but became activated upon irradiation of the corresponding mixtures with 366 nm light. Moreover, the peroxidase activities were switched between relatively fast and slow states multiple times over the course of an oxidation reaction that converted nonfluorescent N-acetyl-3,7-dihydroxyphenoxazine to a brightly fluorescent resorufin derivative. While the detailed mechanism is not yet fully understood, the reported method was found to be general for several peroxidases.

A second example of photoswitchable heterogeneous catalysis took advantage of the reversible, light-induced wettability of TiO$_2$ surfaces.[17] Upon UV irradiation, water molecules in the air may coordinate with the titanium atoms on a TiO$_2$ surface, greatly increasing the number of hydroxyl groups, and thus the hydrogen bonding capability of the surface (Scheme 1).[18] The light-induced change in wettability was confirmed by X-ray diffraction (XRD), Brunauer−Emmet−Teller (BET), and infrared (IR) analyses, as well as contact angle measurements, which collectively indicated that the number of surface hydroxyl groups increased upon UV irradiation and decreased upon standing in the dark. In

Scheme 1. Reversible, UV-Induced Surface Wetting of TiO$_2$ Used to Control the Rate of Aldol Condensations
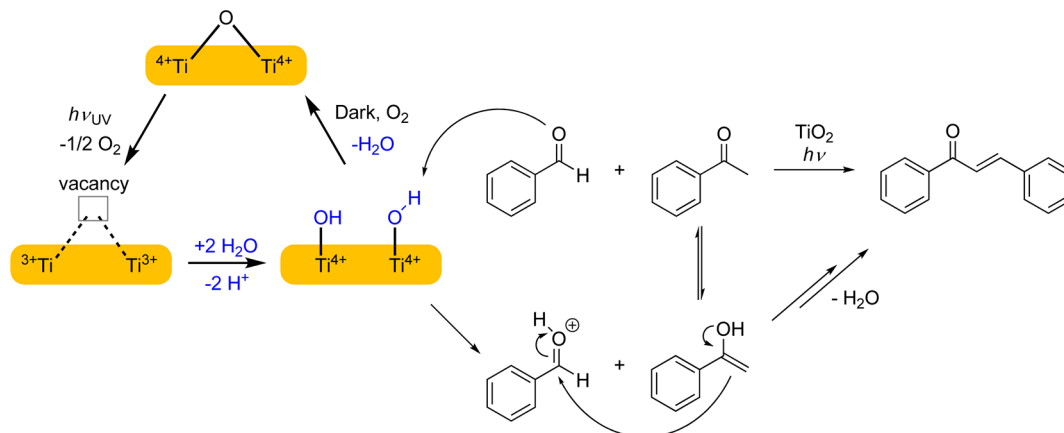
Scheme 2. UV-Induced Ring-Opening of a Nitrospiropyran Triggered Attraction of Negatively Charged Pt NPs to an ITO Electrode and Facilitated Electrocatalytic H$_2$O$_2$ Reduction
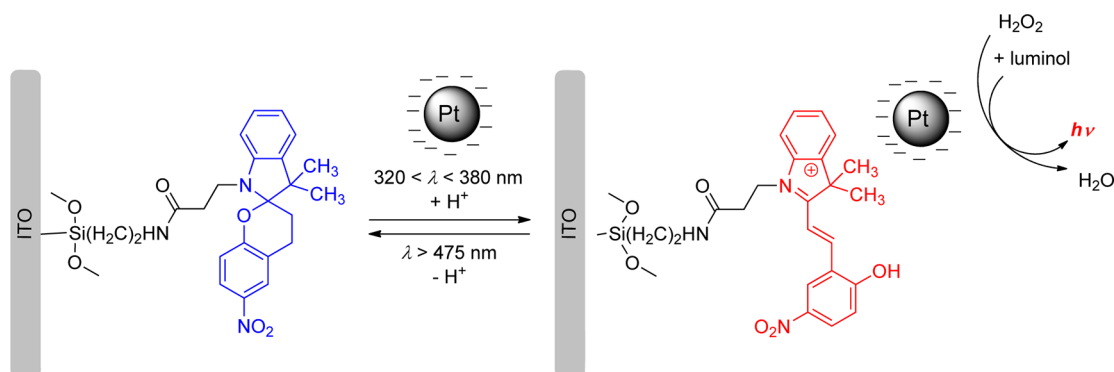
Scheme 3. UV Irradiation of Dispersed Au NPs Decorated with Photochromic Azobenzene Units Resulted in Particle Aggregation and Reduced Catalytic Activity
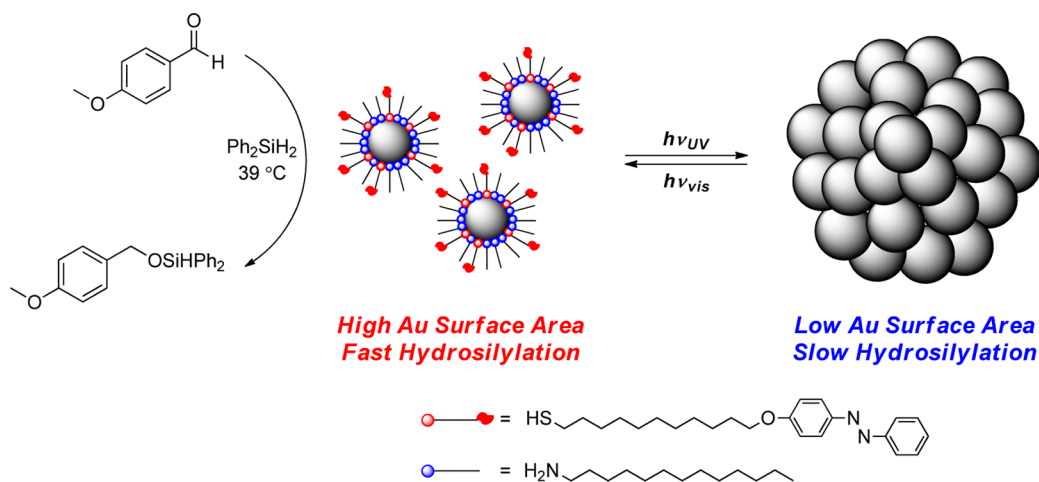
addition, various hydrogen bond catalyzed organic transformations were investigated on these surfaces, including epoxide ring-openings (UV: 33−38% yield; dark: 0−9% yield), cycloadditions (UV: 54−76% yield; dark: 30−34% yield), and C−C forming reactions (UV: 64% yield; dark: 18% yield), and all were found to give higher yields under UV irradiation than in the dark. The reversible wettability was also used to switch the rate of the aldol reaction between benzaldehyde and acetophenone. After the UV-treated TiO$_2$

catalyst was used to promote the reaction (~60% yield), the catalyst was separated and kept in the dark to reduce activity (20% yield). Subsequent irradiation of the TiO$_2$ catalyst with UV light restored the initial catalytic activity (60% yield) when added to a fresh solution of the aforementioned substrates. The irradiation/separation process was repeated up to eight times and consistently displayed higher activities under UV irradiation as compared to analogous catalysts kept in the dark. Collectively, these results demonstrate that photo-

controlled, heterogeneous catalysts, such as TiO$_2$, may be used to modulate a broad range of C−C bond forming and potentially other chemical reactions.

Willner and co-workers[19] reported a unique example of photoswitchable electrocatalysis and chemiluminescence, which utilized Pt nanoparticles (NPs) to reduce H$_2$O$_2$. A photochromic nitrospiropyran derivative was tethered to an indium tin oxide (ITO) electrode to form a monolayer that lacked affinity for the negatively charged Pt NPs, and thus was catalytically inactive toward H$_2$O$_2$ reduction. Upon UV irradiation ($320 < \lambda < 380$ nm) of the system, the nitrospiropyran ring opened to form a positively charged merocyanine species (via concomitant protonation of the corresponding zwitterionic ring-opened product) (Scheme 2). The positively charged monolayer attracted the Pt NPs to the ITO electrode, which facilitated electrocatalytic H$_2$O$_2$ reduction. Subsequent exposure to visible light converted the merocyanine derivative back to the starting spiropyran moiety and resulted in the detachment of the Pt NPs as well as a reduction in catalytic activity. Thus, the ITO electrode was successfully switched between catalytically active and inactive states through alternate exposure to a remote light stimulus. The chemical reaction was detected both electrochemically and via the addition of luminol, which underwent chemiluminescence upon UV irradiation and H$_2$O$_2$ reduction. Notably, the electrocatalytic functions of the electrode could be photoswitched for up to ten cycles without detectable degradation.

Similarly, Gryzbowski and co-workers[20] successfully developed a photoswitchable catalytic system by appending photochromic azobenzene units to NPs. The Au NPs were decorated with a mixed self-assembled monolayer of dodecylamine and azobenzene terminated alkane thiol moieties (Scheme 3). Under ambient light, when the azobenzene units were in the E form, the NPs were readily dispersed in toluene and efficiently catalyzed the hydrosilylation of 4-methoxybenzaldehyde with diphenylsilane. However, upon UV irradiation ($\lambda = 365$ nm) to effect the isomerization of the azobenzene units to their Z form, the NPs aggregated,[21] which reduced the solvent-exposed surface area and significantly slowed the rate of the hydrosilylation reaction ($k_{FAST}/k_{SLOW} = 90$). Subsequent irradiation with visible light resulted in a break-up of the aggregates, redispersion of the particles in solution, and restoration of the initial reaction rate. Using this process, the hydrosilylations were switched between fast and slow states up to three times over the course of a single reaction. The reversible NP aggregation resulted from the development of an electric dipole ($\sim$5 D) caused by the $E \rightarrow Z$ isomerization of the surface azobenzene moieties which, in nonpolar media (i.e., toluene), translated into attractive forces between the NPs. The reversible photoinduced aggregation phenomenon was confirmed by UV−vis spectroscopy, as well as dynamic light scattering and transmission electron microscopy. Taken together, the aforementioned work represented an elegant example of a photoswitchable catalyst that offers large rate differentials as well as repeated switching cycles.

■ HOMOGENEOUS PHOTOSWITCHABLE CATALYSIS

Photoswitchable Sterics. While a number of successful heterogeneous photoswitchable catalysts have been reported, the majority of known systems utilize photochemical processes to modulate the steric properties around the active site of the catalyst. For example, the $E \rightarrow Z$ isomerization of an azobenzene or stilbene moiety[10,11] has commonly been used

to enable steric modulation, as the photoinduced isomerization is accompanied by a significant conformational change. Indeed, Ueno, Takahashi, and Osa reported (1981) the first homogeneous, photoswitchable catalyst by exploiting the UV-induced $E \rightarrow Z$ isomerization of azobenzene in conjunction with a β-cyclodextrin catalyzed ester hydrolysis reaction (Scheme 4).[22] By capping the β-cyclodextrin with an

Scheme 4. Capping β-Cyclodextrin with an Azobenzene Moiety Facilitated Photoswitchable Catalytic Ester Hydrolyses
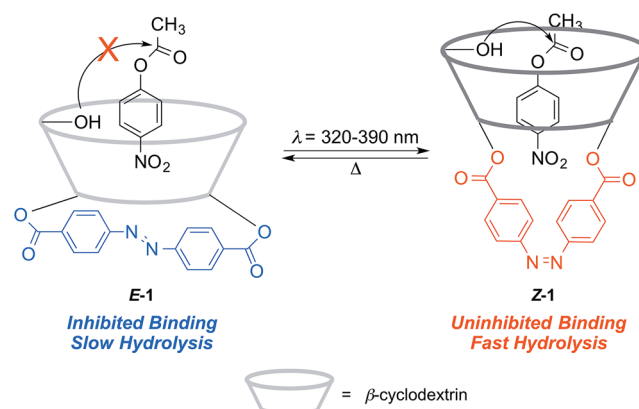

azobenzene moiety, the rate of the hydrolysis of p-nitrophenylacetate was modulated upon exposure of the reaction mixture to UV irradiation. The E-azobenzene appended to the β-cyclodextrin in **E-1** effectively blocked one end of the β-cyclodextrin, and thus prevented strong binding of the ester substrate in the β-cyclodextrin cavity, which inhibited the hydrolysis. Upon UV irradiation ($\lambda = 365$ nm), however, the catalyst isomerized to the Z form, **Z-1**. The corresponding extended β-cyclodextrin cavity promoted substrate binding and resulted in a 5-fold increase in the rate of hydrolysis of p-nitrophenylacetate.

Ueno and co-workers later demonstrated that connecting the azobenzene to the β-cyclodextrin via a histidine spacer facilitated similar photoswitchable catalytic hydrolysis of p-nitrophenylacetate and Boc-alanine-p-nitrophenyl ester due to the differences in steric bulk and binding affinities of the E-azobenzene vs Z-azobenzene moieties ($k_E/k_Z \leq 16$).[23] Furthermore, the azobenzene moieties were later tethered to Au NPs and used in conjunction with β-cyclodextrin as a heterogeneous photoswitchable system to facilitate ester hydrolyses.[24]

In 1995, Rebek and co-workers[25] reported a different photoswitchable catalyst system that relied on the $E \rightarrow Z$ isomerization of azobenzene. The connection of two carbazole-based adenine receptors to an azobenzene moiety enabled control over the rate of the coupling reaction between aminoadenosine **3** and the adenosine-derived ester **4** (Scheme 5). As each receptor unit bound one substrate, **3** or **4**, the disparity in the rates depended on the geometry of the catalyst. The **Z-2** catalyst formed upon UV irradiation ($\lambda = 366$ nm) effectively trapped the substrates in the binding pocket between its two receptor units, allowing them to react efficiently. In the extended **E-2** form, the receptor units and therefore the bound substrates were too distal from each another to react and gave rise to a much smaller coupling rate constant than the folded **Z-2** catalyst ($k_Z/k_E \leq 50$).

Scheme 5. Photochemical Isomerization of Catalyst *E*-2 to *Z*-2 Enhanced the Rate of the Coupling Reaction between 3 and 4
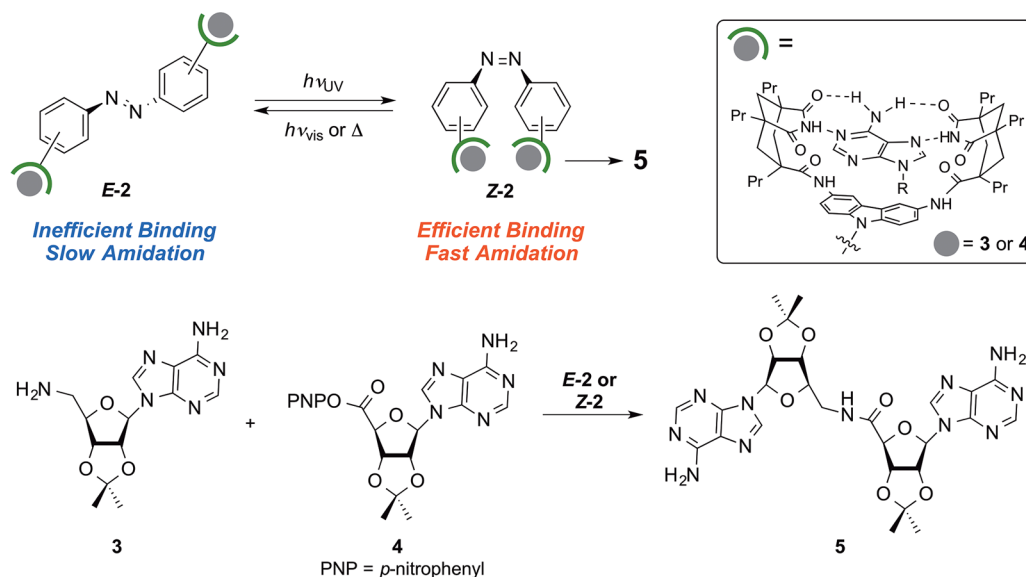
**Scheme 6. Photoswitchable Bis-crown Ether Used to Facilitate Anilide Ethanolyses**
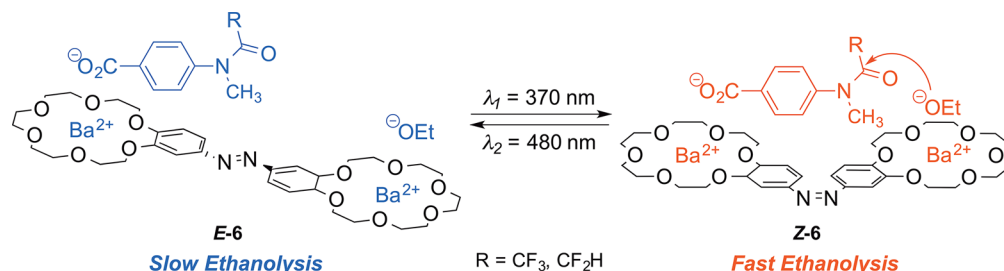
Scheme 7. Unfavorable Steric Interactions between the Porphyrin Ring System and *E*-3,5-di-*t*-butyl-2-stilbazole Prohibited Efficient N−Al Binding and Subsequent Catalytic Activity
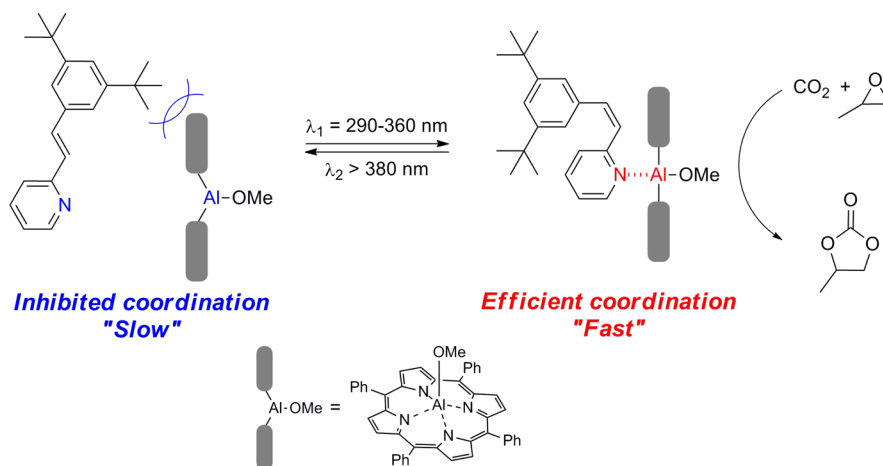
Another elegant example of photoswitching the activity of a supramolecular catalyst using the $E \rightarrow Z$ isomerization of azobenzene was reported by Cacciapaglia and Mandolini.[26] The photochromic azobis(benzo-18-crown-6) **6** was shown to undergo a reversible $E \rightarrow Z$ isomerization upon exposure to UV light (λ = 370 nm) in the presence of bound Ba^{2+} (Scheme 6). Efficient ethanolysis required two metal ions: one to serve as a binding unit for the carboxylate group, and the other to deliver the alkoxide to the amide. Both Ba^{2+} ions were required

to be in sufficiently close proximity to facilitate the attack of the alkoxide, which was only feasible for catalyst *Z*-6 formed upon UV irradiation of the inactive *E*-6 isomer. The reversibility of the isomerization allowed the rate of ethanolysis to be switched multiple times over the course of a single reaction ($k_Z/k_E \leq 5$) by alternating exposure to UV or visible (λ = 480 nm) light.

The reversible photoisomerization of stilbene derivatives has also been employed in photoswitchable supramolecular catalysis. Inoue and co-workers[27] demonstrated that the

Scheme 8. An Azobenzene-Annulated Bis(trityl alcohol) Catalyst Facilitated Control Over a MBH Reaction Using Light
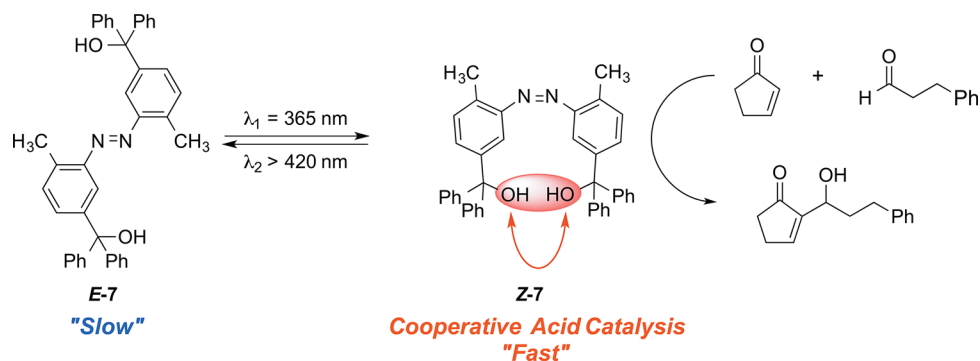
Scheme 9. A Light-Driven Molecular Motor with Integrated Cooperative Organocatalytic Moieties Was Used to Control the Rate and Stereoselectivity of a Michael Reaction
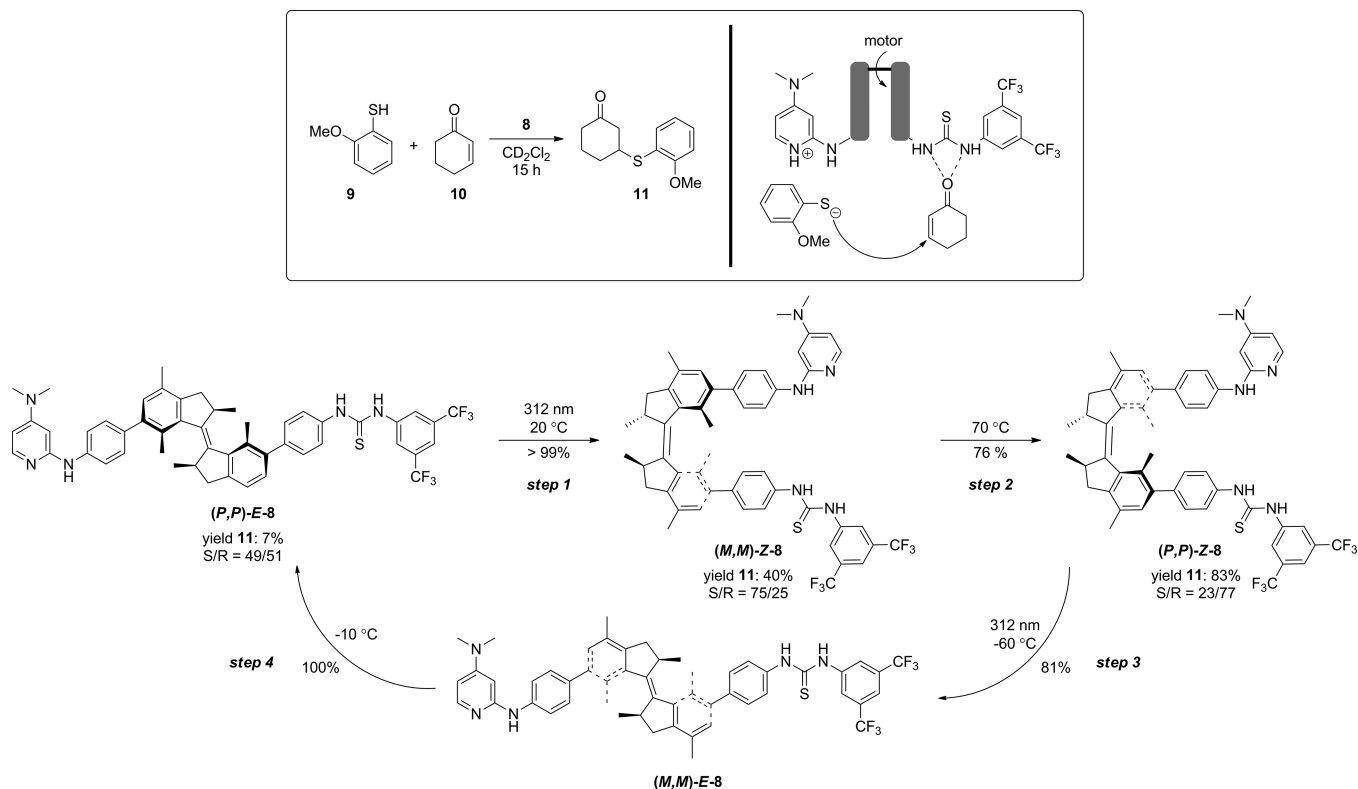
coordination of 2-stilbazole to metalloporphyrins could be reversibly tuned by UV (290 < λ < 360 nm) or visible (λ > 380 nm) irradiation because of the steric differences in the corresponding E and Z isomers. Given that aluminum porphyrin complexes catalyze the condensation of carbon dioxide with epoxides when a nitrogen-containing base is coordinated to the aluminum center, the ability to photochemically tune the nitrogen binding was expected to govern the catalytic activity. Because of unfavorable steric interactions between the porphyrin ring system and the bulky t-butyl groups, E-3,5-di-t-butyl-2-stilbazole was unable to efficiently bind to the aluminum center in methoxyaluminum 5,10,15,20-tetraphenylporphine, resulting in a low yield of propylene carbonate (2% conversion in 18 h; Scheme 7). However, Z-3,5-di-t-butyl-2-stilbazole readily bound to the Al porphyrin and significantly accelerated the formation of product (23% conversion in 18 h). Alternately exposing the aforementioned

system to UV or visible light over the course of the reaction enabled the rate of the condensation to be remotely tuned.

In another example of photoswitchable catalysis, Imahori and co-workers[28] developed an azobenzene-tethered bis(trityl alcohol) for use in the acid-catalyzed Morita−Baylis−Hillman (MBH) reaction (Scheme 8). Similar to the aforementioned supramolecular catalysts, the photoswitchable catalyst 7 relied on cooperative bifunctional catalysis, which can be disrupted by altering the conformation of the catalyst such that the pendant hydroxyl groups are no longer in sufficient proximity to undergo the intermolecular hydrogen bonding needed to increase acidity. Linking two trityl alcohol moieties to an azobenzene core resulted in a cooperative bifunctional catalyst that was photochemically switched between its inactive E form and the active Z isomer. The catalyst Z-7, generated by UV irradiation (λ = 365 nm) of E-7, promoted the MBH reaction of 2-cyclopenten-1-one and 3-phenylpropanal with a 25% increase in reaction yield over its isomer E-7. As a control, the

Scheme 10. Henry Reaction Catalyzed by an Azobenzene Annulated Piperidine upon Photoinduced $E \to Z$ Isomerization
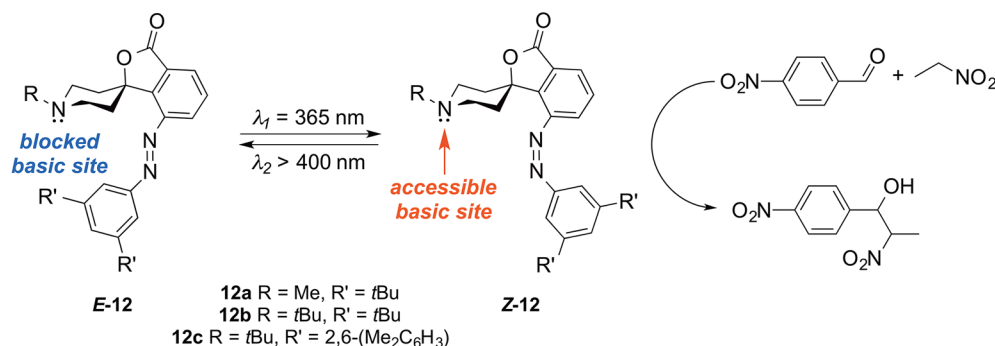
reaction catalyzed by trityl alcohol proceeded with negligible conversion, indicating that both trityl alcohol units were needed to promote the reaction, which further supported the notion that the photochemically induced change in spatial arrangement was responsible for the observed reactivity differences.

Photoswitchable supramolecular catalysis was later expanded by Feringa and co-workers to control both catalytic activity as well as stereoselectivity via a light-driven molecular motor.[29] Incorporation of two organocatalytic moieties, a dimethylaminopyridine (DMAP) Brönsted base and a hydrogen bonding thiourea, into a unidirectional molecular rotary motor[30] provided a means to photochemically alter the stereochemical outcome of a catalytic reaction in a sequential manner. The clockwise rotation of the rotor in **8** (Scheme 9) was confirmed by a combination of chiral HPLC, as well as UV−vis, circular dichroism (CD), and ^{1}H NMR spectroscopy. When the (P,P)-**E-8** isomer was used as a catalyst, the Michael addition of 2-methoxylthiophenol **9** to cyclohexenone **10** proceeded slowly (7% conversion in 15 h) to give a racemic mixture of the expected product **11** due to the unfavorable orientation of the DMAP and thiourea moieties on the catalyst. Upon UV irradiation (λ = 312 nm), however, to effect the isomerization to the (M,M)-**Z-8** isomer, the rate of the Michael reaction was significantly enhanced (40% conversion in 15 h), and the S enantiomer of **11** was preferentially formed with an enantiomeric ratio (e.r.) of 75/25 S/R. The Z isomer of opposite helicity, (P,P)-**Z-8**, which was formed by heating (M,M)-**Z-8** to 70 °C, exhibited an even higher reaction conversion (83% yield of **11** in 15 h) and concomitant inversion of the enantioselectivity (e.r. 23/77 S/R). The cooperative catalysis involved concerted activation of the enone by the thiourea and deprotonation of the thiol by the DMAP to facilitate the 1,4-addition; thus, the molecular rotation of the catalyst ultimately controlled the stereoselectivity of the reaction. Moreover, the helicity of the catalyst determined the absolute stereochemistry of the product because of the steric hindrance of the si face of the enone in the transition state involving (P,P)-**Z-8** as opposed to hindrance of the re face of the enone when (M,M)-**Z-8** was used. The aforementioned molecular motor catalyst is exceptional as it allows for control over catalytic activity as well as stereoselectivity in a reversible and sequential manner using temperature and light stimuli.

Departing from photoswitchable supramolecular catalysis, Hecht and co-workers[31] adapted the concept of photoreversible steric shielding to small molecule catalysts by incorporating an azobenzene unit into a piperidine base. In the elegantly designed, conformationally restricted, N-alkylated piperidine **12**, the lone pair of electrons on the nitrogen atom may be

reversibly blocked by the azobenzene substituents (Scheme 10). The shielding was optimized through the introduction of structural restrictions, including the predominance of the chair conformation with the N-alkyl substituent in the equatorial position, the spiro junction fixing the azobenzene moiety, and the steric bulk of the 3,5-disubstituted phenylazo group. The resting catalyst **E-12** featured a sterically inaccessible basic site and exhibited a fairly low basicity in titration experiments with trifluoromethanesulfonic acid. However, UV irradiation (λ = 365 nm) effected an isomerization to form **Z-12**, which left the basic site accessible and significantly increased the catalyst's basicity (pK_a(**Z-12c**) − pK_a(**E-12c**) = 0.7). X-ray crystallography unambiguously revealed the preferred chair conformation and the position of the azobenzene substituent, which effectively shielded the N lone pair in the E-isomer but not in the Z-isomer.[32] As a result of the photoisomerization, **E-12c** displayed negligible catalytic activity in the aza-Henry reaction between p-nitrobenzaldehyde and nitroethane, while **Z-12c** efficiently promoted the reaction (k_Z/k_E = 35.5).[29] In a subsequent study, the aforementioned piperidine was immobilized on silica and used as a heterogeneous photoswitchable catalyst.[33]

While the $E \to Z$ isomerizations of azobenzene and stilbene moieties have been widely used as steric photoswitches for a variety of catalysts, Branda and co-workers[34] took advantage of a dithienylethene photocyclization to alter the steric properties of a copper(I) cyclopropanation catalyst. A chiral bis(oxazoline) dithienylethene ligand was developed which, in its open form (**13o**), was capable of chelating a Cu(I) atom in the chiral pocket between the two oxazoline moieties to facilitate the enantioselective cyclopropanation of styrene (30−50% ee; Scheme 11). Upon UV irradiation (λ = 312 nm), however, the bis(oxazoline) ligand ring-closed to form **13c**, wherein the oxazoline moieties were too far apart to chelate a copper atom. Thus, when the photocyclized ligand **13c** was used in the cyclopropanation reaction, negligible enantioselectivity was observed (5% ee). Subsequent irradiation with visible light (λ = 434 nm) effected the cycloreversion to **13o** and restored the enantioselectivity, thus demonstrating the first example of photoswitching the stereoselectivity of a copper catalyzed reaction.

Photoswitchable Electronics. While a number of photoswitchable catalysts have successfully employed changes in steric properties to alter catalytic activities, the ability to photomodulate the electronic properties of the active site of a catalyst offers potential for remote tuning of chemo- and/or regioselectivity, as well as activity. Diarylethenes hold significant promise in this regard, as their photocyclization results in a

Scheme 11. Chelation of a Cu(I) Atom in the Chiral Pocket of 13o Facilitated Stereoselective Cyclopropanations; UV Irradiation to Form 13c Disrupted the Cu Chelation and Decreased the Stereoselectivity
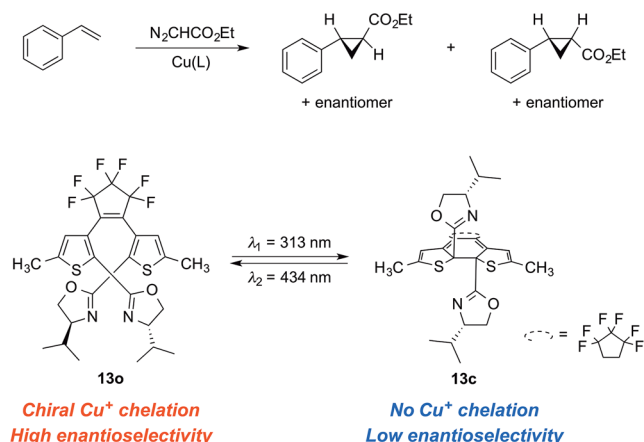
redistribution in electron density when exposed to UV irradiation, which may be reversed upon treatment with visible light. The resulting changes in electronic properties have led to differences in a variety of chemical properties,[35] including acidity,[36] basicity,[37] hydrogen bonding,[38] ligand coordination,[39] and propensity to undergo cycloaddition chemistry.[40] Only in a few instances, however, have such photoinduced electronic changes been harnessed in catalytic applications.

An excellent example of photoswitching catalytic activity via electronic modulation was reported by Branda and co-workers.[41] Drawing inspiration from using light to control biochemical processes, a photoresponsive mimic of the biologically active form of vitamin B_6, pyridoxal 5′-phosphate (PLP) was developed. The action of PLP is dependent upon the electronic connection of the aldehyde and pyridinium functional groups. The pyridinium group in the aldimine generated by condensation of an amino acid with PLP enhances the acidity of the α-hydrogen via stabilization of the conjugate base through contributions from the quinonoid resonance structure (Scheme 12). A photoresponsive PLP analogue was developed by replacing the PLP core ring with a photochromic diarylethene unit where, in the ring-open form 14o, the pyridinium and aldehyde units were electronically isolated from each other, which precluded catalytic activity. However, UV irradiation (λ = 365 nm) to form the ring-closed isomer 14c resulted in a fully conjugated structure in which the pyridinium and aldehyde groups were electronically connected. In this case, the ring closed isomer 14c was therefore able to form the stabilized quinonoid structure upon condensation with an amino acid followed by deprotonation of the aldimine α-hydrogen. Indeed, treatment of L-alanine with 14o resulted in no reaction; however, upon UV irradiation to form 14c, an immediate surge in the rate of racemization was observed, which was later attenuated by subsequent exposure to visible light. It was therefore possible to switch the catalyst between its

**Scheme 12. Photoresponsive PLP Mimic for the Photoswitchable Racemization of L-Alanine**
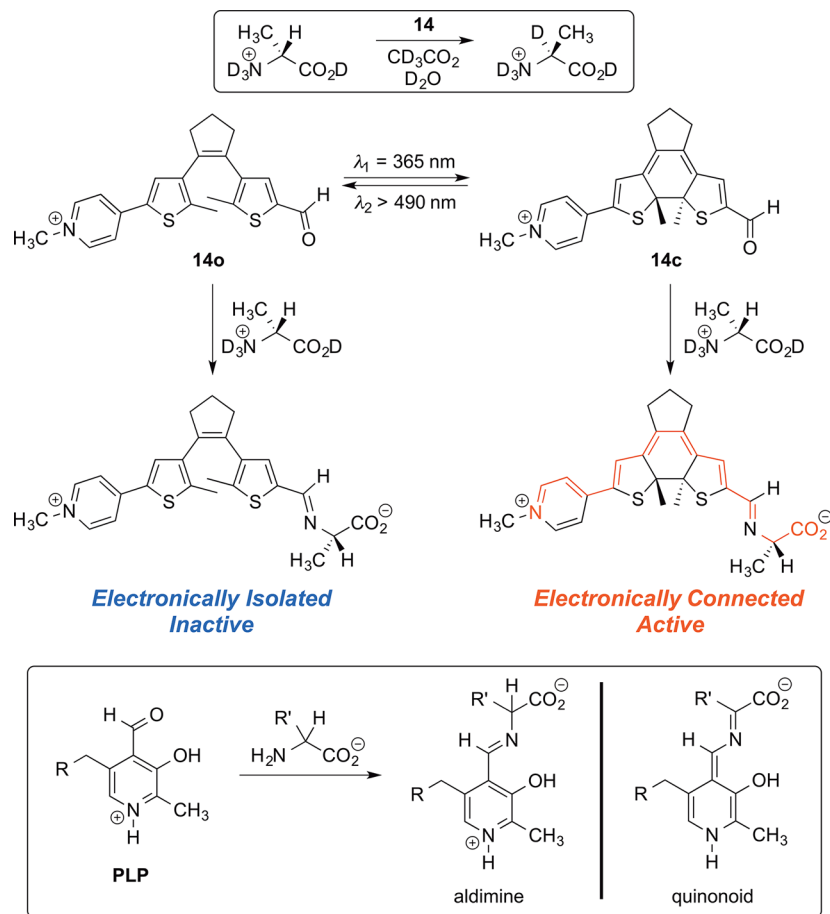
Scheme 13. Ring-Open Isomer 15o of a DTE-Annulated NHC Facilitated Transesterifications, Amidations, and ROPs in Ambient Light, Whereas the Corresponding Reactions Were Inhibited upon Photoinduced Formation of Ring-Closed Isomer 15c
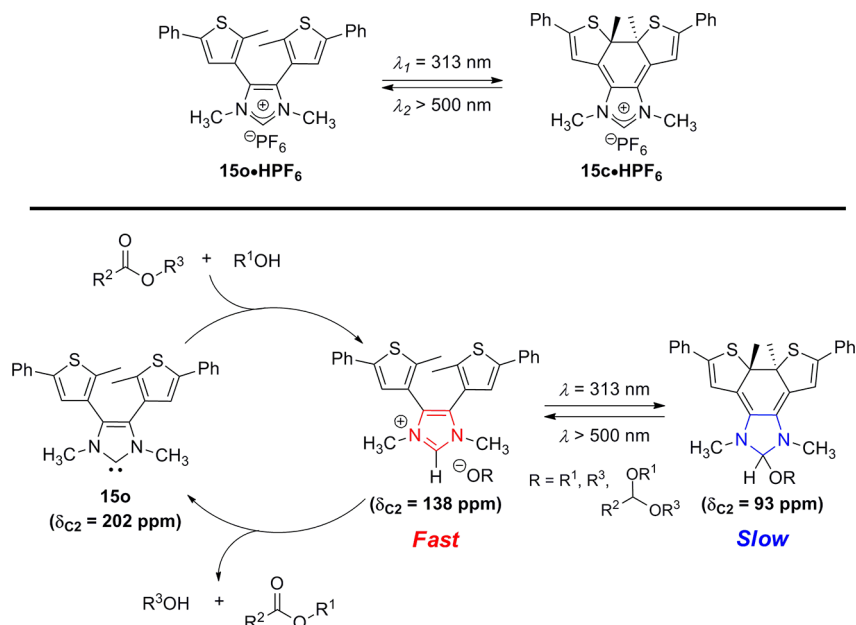
Scheme 14. Rh(I) Catalyst Featuring a DTE-Annulated NHC Ligand Enabled Photoswitchable Hydroborations
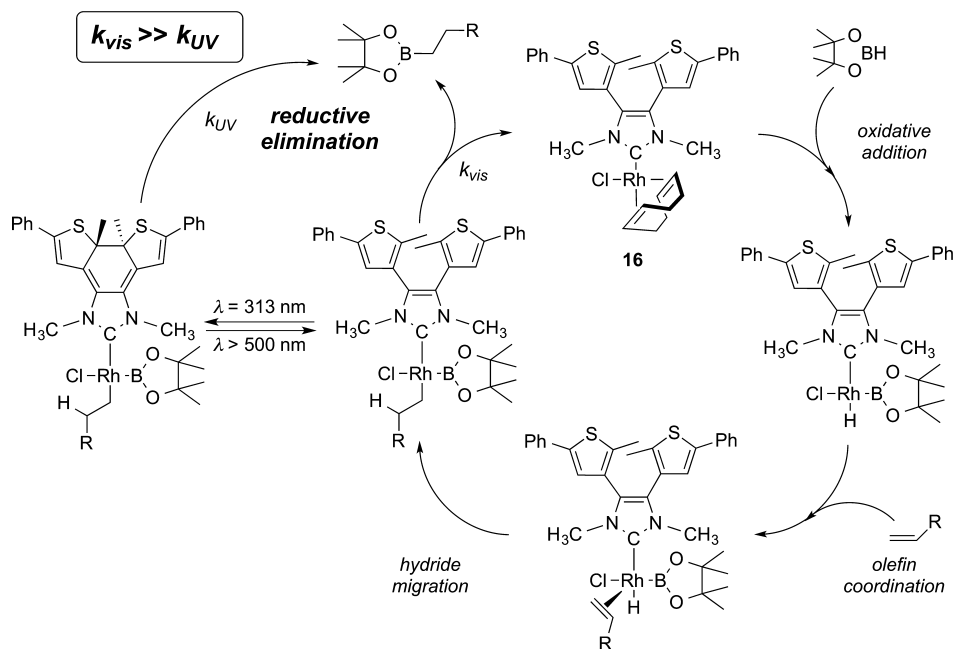
inactive form **14o** and its active form **14c** through alternate exposure to UV and visible light ($\lambda > 490$ nm).

Another example of photomodulating catalytic activity via changes in electronics was recently reported by our group.[42] Building on earlier results which showed that the photocyclization of a dithienylethene (DTE) properly annulated to a N-heterocyclic carbene (NHC) scaffold decreased the electron density at the carbenoid center in imidazolium salts[43] and other NHC adducts,[44] we prepared the DTE-annulated NHC precatalyst[45] **15o•HPF$_6$** (Scheme 13). This imidazolium salt was shown to undergo the expected electrocyclic ring-closing under both neutral and basic conditions upon exposure to UV

irradiation; subsequent exposure to visible light reversed the reaction. Under ambient light and in the presence of base, **15o•HPF$_6$** efficiently catalyzed transesterification[46] and amidation[47] reactions. However, upon exposure to UV irradiation, the rate of the condensation of vinyl acetate with allyl alcohol was significantly attenuated ($k_{\text{vis/UV}} = 12.5$), as was the rate of the amidation of ethyl acetate with 2-aminoethanol ($k_{\text{vis/UV}} = 100$). The rate of the amidation reaction was successfully toggled between fast and slow states by alternating exposure to UV and visible irradiation over the course of the reaction. Moreover, through NMR studies, in which the C2 carbon in **15o•HPF$_6$** was isotopically labeled with a ^{13}C atom,

revealed that the resting state of the active catalyst was an imidazolium species which converted to an inactive NHC alcohol adduct upon UV irradiation and photocyclization. Subsequent irradiation with visible light reversed the photocyclization and converted the NHC-alcohol adduct back to the active imidazolium species, which re-engaged the catalytic cycle.

The same NHC precatalyst was also applied to control the ring-opening polymerizations (ROPs) of cyclic esters, including ε-caprolactone and δ-valerolactone, using light.[48] The ROPs were promoted by **15o** in ambient light; however, UV irradiation to form the photocyclized catalyst, **15c**, resulted in significant attenuation of the polymerization rate (k_{amb}/k_{UV} = 59 for δ-valerolactone). Moreover, the ROP of δ-valerolactone could be reversibly activated and deactivated over the course of a polymerization reaction through alternate exposure to visible and UV light. While photoactivated catalysts for ROPs were previously reported,[49,50] as were photoswitchable radical polymerizations,[51] **15o** was the first example of a photoswitchable ROP organocatalyst, as well as the first photoswitchable NHC-based polymerization catalyst. Given the versatility of NHCs for facilitating various ROPs and other polymerizations,[52] the method may be extended to a wide variety of monomers for the development of novel materials with sophisticated macromolecular architectures and advanced functions.

The ability to photomodulate the donicity of an NHC was later extended to enable photoswitching of the intrinsic catalytic properties displayed by a Rh(I) complex.[53] Complex **16**, which featured a DTE-annulated NHC ligand (Scheme 14), underwent the expected photocyclization upon UV irradiation and decreased the donating ability of the NHC. The photocyclization and accompanying decrease in ligand donicity were both reversed upon subsequent exposure to visible light. Complex **16** satisfied an important requirement for photoswitchable catalysis in that its photochemistry was found to be robust, in contrast to many other photochromic metal complexes, which are often susceptible to photodegradation.[54] Under ambient light, **16o** efficiently promoted the hydroboration of alkenes and alkynes;[55] in contrast, exposure to UV light (λ = 313 nm) attenuated the reaction rates by up to an order of magnitude. Notably, the hydroboration of styrene with pinacolborane could be photoswitched multiple times over the course of the reaction via alternate exposure to visible and UV irradiation. The rate attenuation upon exposure to UV light was attributed to the decrease in donicity of the NHC ligand upon photocyclization, which inhibited the rate-determining reductive elimination step of the corresponding hydroboration catalytic cycle (Scheme 14). Complex **16** constituted the first example of photomodulating catalytic activity via a change in ligand donicity and established a new concept in homogeneous catalysis. Given the vast array of transformations catalyzed by NHC-supported metal complexes,[56] the method described above may be extended to a variety of other reactions and offers new opportunities to facilitate multiple, mechanistically-distinct reactions using a single catalyst.[57]

PERSPECTIVES

While a number of notable accomplishments have been achieved, the growing field of photoswitchable catalysis faces several challenges. The practical utility of photoswitchable catalysts hinges on the continued development of catalytic species that can be converted with high fidelity between two significantly sterically or electronically different states. A need

also remains for photoswitchable catalysts that can convert rapidly, with high conversions, without decomposition, and at desirable reaction concentrations ($\sim$0.1−1.0 M) to maximize the number of possible switching cycles. Furthermore, catalysts that can be switched using less energetic and more readily accessible wavelengths of light (i.e., visible light) would significantly enhance their synthetic utility. Relay photoswitchable catalysts that utilize visible light absorbing chromophores to emit light of shorter wavelengths to the catalytic unit would offer great potential to preclude the need for external UV sources, and potentially to circumvent the low reaction concentrations required for most known photochromes. Moreover, the design of more versatile and/or synthetically relevant catalysts is still desirable, given that many of the known photoswitchable catalysts are only able to mediate a small number of transformations. Olefin metathesis, C−C bond formations, and polymerizations catalyzed by homogeneous metal catalysts, nucleophilic organocatalysts, and/or general acid/base catalysts are all attractive targets for photoswitchable catalysis. While a number of these have been reported, catalysts that broaden the scope of possible synthetically relevant transformations would be valuable.

Ultimately, photoswitchable catalysis will require the ability to photochemically alter the selectivity of the catalyst in addition to its activity. A system in which the catalyst's intrinsic chemo-, regio-, and/or stereoselectivity could be remotely photomodulated will have numerous applications in tandem catalysis,[57] and is expected to provide unprecedented control over polymer microstructure, as well as to simplify multistep syntheses of complex small molecules. Current methods provide an understanding of how catalyst activity (i.e., reaction rates) may be controlled by using light and establish the foundation for modulating catalyst selectivity, since achieving chemo-, regio-, and stereoselectivity relies on the ability to facilitate one reaction pathway while suppressing another. Developing catalysts with photoswitchable selectivities will require methods to more finely tune the steric or electronic properties of a catalyst's active site to specifically control how the catalyst interacts with different substrates and intermediates during the catalytic cycle. A promising approach to this attractive, while daunting, challenge is to expand the development of photoswitchable ligands[38] that enable photomodulation of the steric environment or electronic character of the ligated catalytic metal center. Despite often low photochemical conversions and photodegradation,[53] the use of photochromic metal complexes as photoswitchable catalysts would expand the scope of applicable reactions, and offer potential for switching reactant or product selectivities through precise tuning of the active site (i.e., the metal center).

CONCLUSIONS

In summary, the field of photoswitchable catalysis has seen rapid development over the past three decades. A variety of conceptually different approaches have been utilized to reversibly control chemical transformations using light. For example, heterogeneous photoswitchable catalysis has been realized using photosensitive surfaces, such as TiO_2 and CdSe. The attachment of photochromic moieties to such surfaces is also possible and capable of rendering them photoswitchable, a concept that may be extended to other solids. Additionally, a number of photoswitchable homogeneous catalyst systems have been realized by capitalizing on the steric changes resulting from the photochemical $E \rightarrow Z$ isomerization of azobenzene

and/or stilbene derivatives. Photochromic diarylethene moieties have also been incorporated into catalytic systems to facilitate switching of stereochemistry through steric changes and catalytic activity via alteration of a catalyst's electronic properties. While significant advances have been made, continuing efforts in the field are expected to focus on developing robust, broadly applicable photoswitchable catalysts to enable the fine-tuning of reaction selectivity, to expedite multistep and tandem syntheses, and to enrich the structures and functions of polymeric materials.

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Notes
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