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FEATURE ARTICLE

Manipulating excited state reactivity and selectivity through hydrogen bonding – From solid state reactivity to BrØnsted Acid Photocatalysis

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Hydrogen bonding mediated control of photochemical reaction is highlighted with an eye towards the development of BrØnsted Acid mediated photocatalysis.

Introduction

The role of hydrogen bonding in evolution is quite fascinating. Recognizing this critical non-bonding interactions in biological systems, chemists have developed hydrogen bonding motifs to regulate self-assembly and control chemical reactivity.[1-4] In this feature article we will be highlighting the role of hydrogen bonding templates (Figure 1) to control excited state processes both in solid-state and in isotropic media with an eye towards appreciating BrØnsted acid mediated photocatalysis.[2-4]

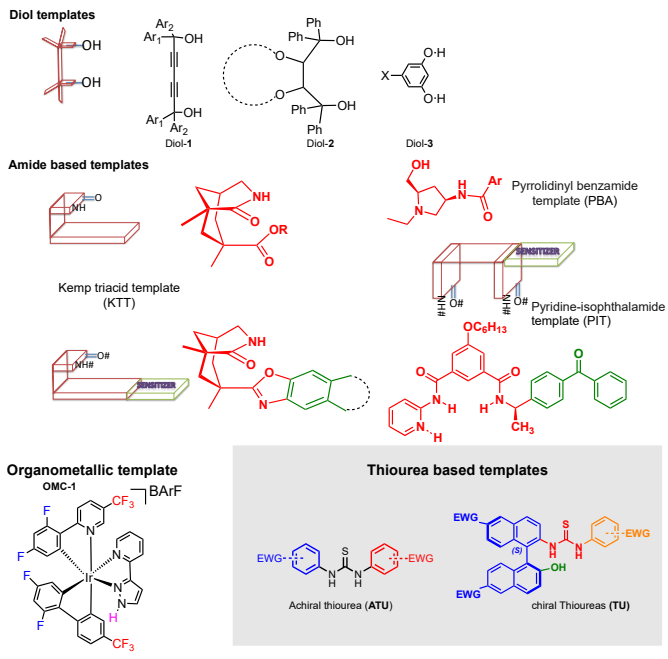
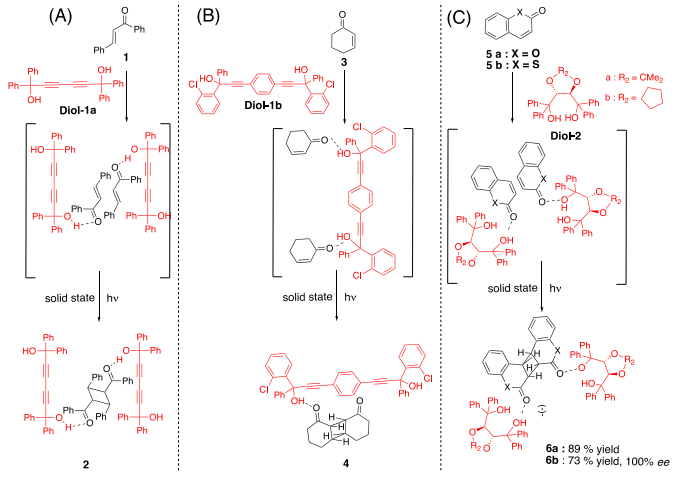


Figure 1: Hydrogen bonding templates for controlling excited state transformations.

Hydrogen bonding templates to control photochemical reactivity in solid state

One of the seminal work in the area of hydrogen bonding template mediating photochemical transformations in the solid-state[5-9] was reported by Toda, Tanaka and co-workers.[10-17] Diols such as diyne-diols **Diol-1a** and **Diol-1b** (Scheme 1A-B) as well as chiral **Diol-2** derived from tartaric acid (Scheme 1C) were employed to pre-organize olefins (e.g. chalcones, coumarins) towards photodimerization in the solid-state.[10, 11] For example, photoirradiation of powdered complex of chalcone **1** with diacetylene diol host **Diol-1** resulted in *syn-head-tail* (HT) dimer as the major product with > 80% yield (Scheme 1A). Employing a chiral **Diol-2** for photodimerization of coumarin **5a** and thiocoumarin **5b** led to the corresponding enantioenriched photoproducts with excellent yield and high optical purity (~100% *ee*) in the solid state (Scheme 1C).



Scheme 1: Hydrogen bonding diols as crystalline hosts for photochemical transformations in the solid state.

Nakamura and co-workers[18] utilized coumarin motif as part of the hydrogen bonding template that was derived from Kemp triacid (**KTT1**). The **KTT1** template served both as a light-absorbing motif as well as an anchoring unit to facilitate

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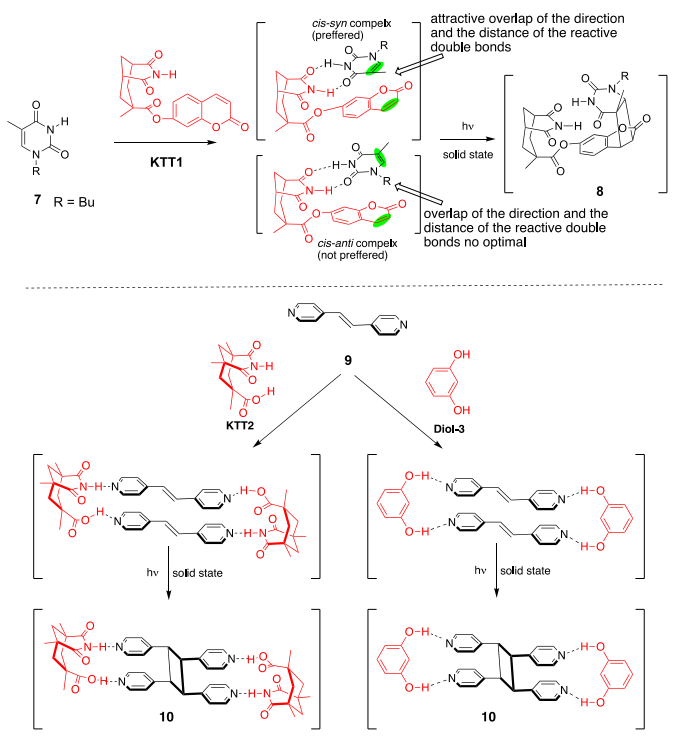
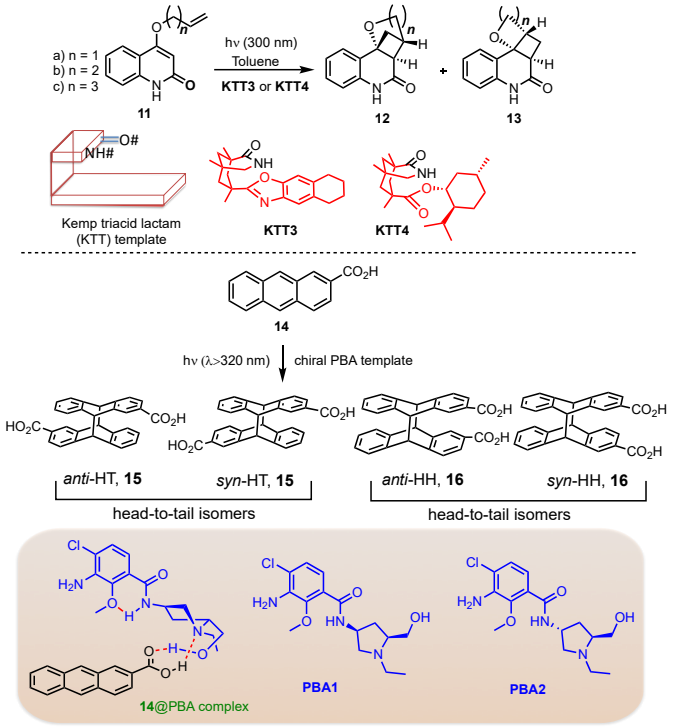
photocycloaddition with thymine **7.** The hydrogen bonding interaction coupled with facial differentiation during photoreaction led to the exclusive formation of *cis-syn*-adduct **8**. The formation of *cis-syn*-adduct was postulated to occur through a "*cis-syn*-complex" that featured favorable interactions due to "ππ–stacking" when comparted to "*cis-anti*-complex". This led to an attractive overlap of the direction and the distance of the reactive double bonds leading to the formation of *cis-syn*-adduct **8** (Scheme 2). MacGillivray and co-workers employed resorcinol (1,3-dihyroxybenzene) **Diol-3** as a host template to control photochemical reactivity of molecules in the solid-state.[19-21] Olefins featuring pyridyl rings (e.g., **9**) were templated towards photodimerization in the solid-state (Scheme 2) leading to photoproduct **10** with excellent control of reactivity. Similar strategy was also extended to other olefins such as pyridylethylenes, dienes and trienes.[21, 22] They also employed the Kemp triacid derived template **KTT2** for dimerization of **9** (Scheme 2) leading to selective formation of photoadduct **10**.[23] While H-bonding directed reactivity in crystalline media gave insights into molecular reactivity, it was not generally applicable to compounds that are not crystalline. In addition, translating the interactions for asymmetric photoreactions for a diverse set of compounds necessitated that the strategy has to be extended to solution phase reactions with the knowledge gained from solid-state studies.



Scheme 2: Dimerization of dienes and trienes templated using hydrogen bonding hosts.

H-bonding templates for controlling enantioselective photochemical transformations in solution

One of the recent advances by photo chemists is to utilize hydrogen-bonding templates for controlling enantioselective photochemical transformations in isotropic media (Scheme 3). Bach and co-workers have extensively utilized Kemp triacid derived templates (**KTT3**-**KTT6**; *cf.* Schemes 3 and 4) to control photochemical transformations and to achieve stereoselectivity in solution.[24-27] Kemp triacid lactam template (+)-**KTT3** or (-)-**KTT4** were utilized for controlling the enantioselective transformations of 4-substituted quinolone **11** (Scheme 3).[24] [2+2]-Photocycloaddition reactions of quinolone **11a** with Kemp triacid lactam templates (-)-**KTT4** (Scheme 3) resulted in low enantioselectivity of 37% in the photoproduct **12a** with 89% yield at -15 °C in toluene. The weak association between **11** and (-)-**KTT4** when compared to (+)-**KTT3** was rationalized for the observed low and high enantioselectivity with the two hosts. The enantioselectivity increased to 93% (77% yield) when 2.6 equivalents of (+)-**KTT3** was employed at -60 °C. Photocycloaddition of quinolone **11c** featuring a longer alkyl chain with 1.2 equivalents of chiral host (+)-**KTT3** in toluene at -15 °C resulted in 88% enantioselectivity with 88% yield. In spite of not being sub-stochiometric, the study clearly provided a guide for employing hydrogen bonding templates for enantioselective transformations in isotropic media.



Scheme 3: Hydrogen bonding templates for controlling stereoselective phototransformations in solution.

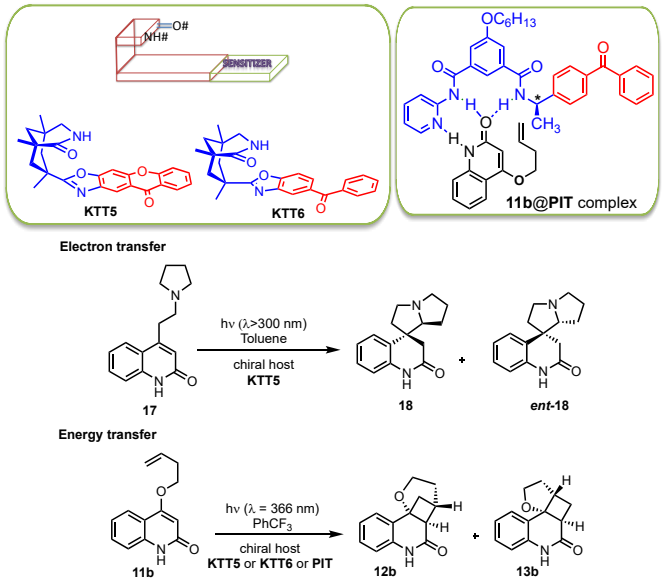
Inoue and co-workers[28] utilized pyrrolidinyl benzamide (**PBA**) derived chiral H-bonding template (Scheme 3) for controlling enantioselective photodimerization of anthracene-carboxylic acid **14**. Photodimerization of **14** was evaluated in the presence of **PBA** template in dichloromethane at two different temperatures (25 °C and -50 °C). **PBA1** template featuring *cis* geometry between amide and alcohol functionality gave 25-43% enantioselectivity in the *syn*-HT-**15** photoproduct and 10-43% enantioselectivity in the *anti*-HT-**15** photoproduct. Low enantiomeric excess (<3 % *ee*) of photoproducts were observed when **PBA2** template that featured a *trans* geometry between amide and alcohol functionality. Based on the single crystal XRD

analysis of the **PBA-14** complex, the authors reasoned that the interaction of the **PBA** template with the **14** in the hydrogen-bonded complex led to a preferential attack from the open enantioface of the **14** bound to the chiral template. Thus, the study clearly established the geometric features (*cis*/*trans* relation) in **PBA1** and **PBA2** being crucial in the stereo-differentiation processes.

Sensitizing H-bonding templates for enantioselective phototransformations

The hydrogen bonding template also served as a sensitizing unit enabling energy transfer or electron transfer.[25-27] Appending a hydrogen bonding template to a sensitizer provides an avenue to bring the reactive substrate(s) in close proximity, enabling energy or electron transfer leading to efficient photochemical reactivity coupled with stereodifferentiation.

Krische and co-workers[29] utilized benzophenone triplet sensitizer that was appended to a chiral pyridine-isophthalamide template (**PIT**) for performing enantioselective [2+2]-photocycloaddition of quinolones **11b** (Scheme 4). Hydrogen bond enabled host-guest complex formation between the template and the substrate was rationalized for the enhanced photoreactivity of **11b** in the presence of 0.25–2 equivalents of the **PIT** template in $CDCl_3$ at -70 °C. The reaction mechanism was postulated to occur through triplet energy transfer from benzophenone to the substrate that led to enhanced photoreactivity. In spite of the increased photoreactivity, low enantiomeric excess of ~20% was observed in the photoproduct **12b** (Scheme 4).



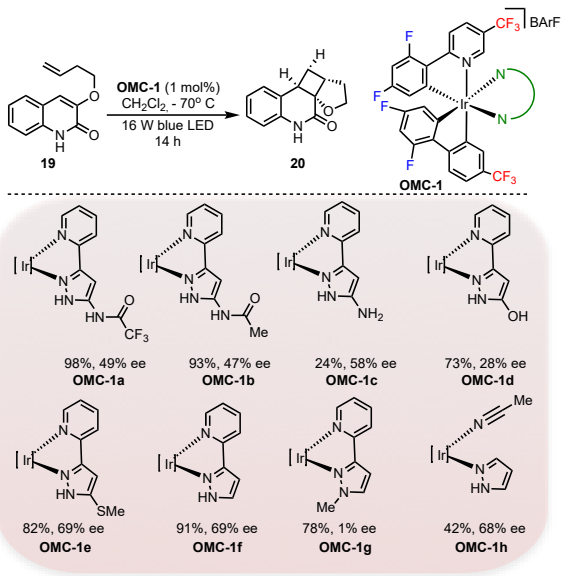
Scheme 4: Sensitizing Hydrogen bonding templates for controlling electron transfer and energy transfer mediated enantioselective phototransformations.

Bach and co-workers[25-27] utilized chiral sensitizers appended to Kemp lactam host for both electron and energy transfer mediated phototransformations (Scheme 4).[25-27] They employed xanthone appended Kemp lactam host **KTT5** for photoinduced electron transfer reaction with quinolone **17** (Scheme 4) leading to 70% enantioselectivity with 64% yield of the photoproduct **18**. The mechanism involved a photo-induced electron transfer followed by a proton transfer leading to the formation of diradical intermediate(s), that cyclized to form **18**.

Bach and co-workers[25-27] also extended the strategy for energy transfer initiated intramolecular [2+2]-photocycloaddition of quinolone **11b.** With benzophenone appended host **KTT6** (10-mol%), low enantioselectivity of 39% was observed in photoproduct **13b** at -25 °C. On the other hand, xanthone appended host **KTT5** (5 mol%) gave high enantioselectivity of 90% in the photoproduct **13b**. The regioisomeric ratio was 79:21 for the photoproducts **12b**:**13b**. In both the cases, the reaction mechanism involved triplet energy transfer leading to diradical intermediates en route to the formation of the photoproduct. The absorptivity and low triplet energy of benzophenone when compared to xanthone was highlighted to be a crucial factor for the observed difference in stereoselectivity between the two templates.

Organometallic complexes as hydrogen bonding templates for photoreactions

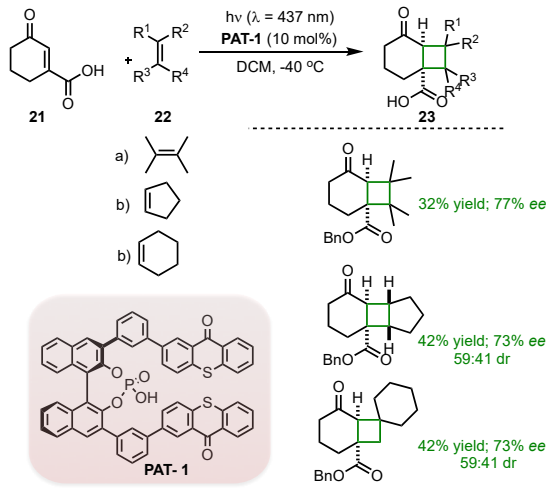
Based on the report by Meggers and co-workers[30] on employing Iridium (III) photocatalysts bearing electron-deficient cyclo-metalated phenyl pyridine, Yoon and co-workers[31] employed ligands featuring BrØnsted acidic sites for hydrogen-bonding asymmetric photocatalysis. They revealed the intramolecular photocycloaddition of 3-alkoxyquinolone **19** that featured low triplet energy that was amenable to energy transfer from Iridium based organometallic catalyst **OMC-1a** at 1 mol% loading with blue LEDs at −70 °C leading to photoproduct **20** in 98% yield with an enantioselectivity of 49% (Scheme 5). Both the thiomethyl-substituted catalyst **OMC-1e** and the unsubstituted catalyst **OMC-1f** gave 69% enantioselectivity in the product **20**.



Scheme 5: Organometallic hydrogen bonding motifs for enantioselective [2+2]-photocycloaddition

Phosphoric acid based hydrogen bonding templates for organo-photocatalysis

Bach and co-workers utilized chiral phosphoric acid template **PAT-1** to evaluate asymmetric inter-molecular [2+2] photocycloaddition of cyclic enones **21** (Scheme 6) with different alkenes **22a-c**.[32] This **PAT-1** template featured two thioxanthone moieties connected to a 2,2'-binapthol system at the 3,3' position. Photoirradiation of enone **21** and alkene **22a-c** in the presence of **PAT-1** catalyst led to the corresponding cyclo-adducts **23a-c** with reasonable yields (30-40%) and good enantioselectivity (70-80% *ee*). Bach and co-workers also explored the mechanism by NMR studies and DFT calculations and proposed that the enantioface differentiation through triplet energy transfer that was promoted by hydrogen bonding mediated interactions between **PAT-1** photocatalyst and enones **21** (Scheme 6).

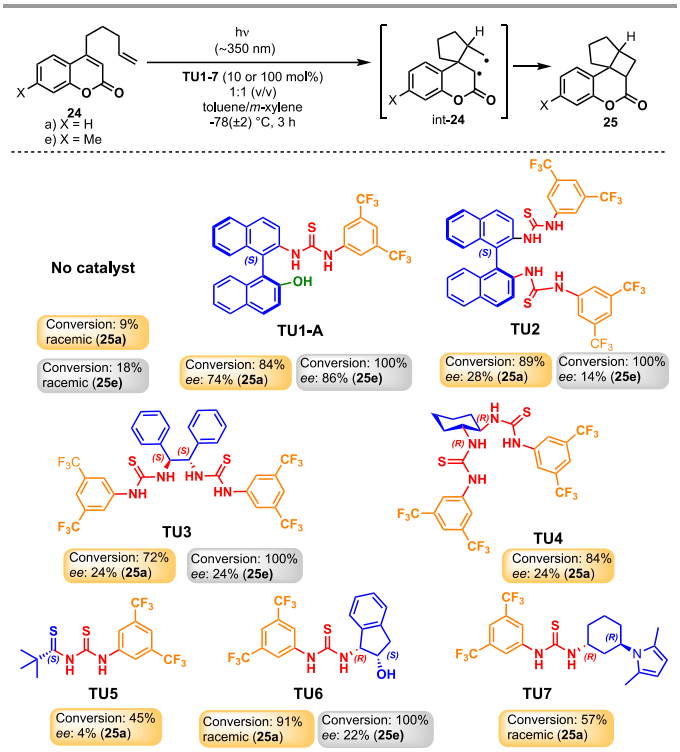


Scheme 6: Chiral Phosphoric acid as organophotocatalyst for intermolecular [2+2] cycloaddition.

Thiourea based hydrogen bonding templates for organo-photocatalysis

While the hydrogen bonding templates reviewed above were very effective for enantioselective phototransformations, a systematic investigation for manipulating the stereo-electronic features of the organo-photocatalyst (similar to ground state reactions) for asymmetric phototransformation was lacking. It became critical to perform an in-depth study of photophysical and photochemical features and how the energetics and dynamics in the excited state impacts designing of novel organo-photocatalysts for excited state transformations.[33-35] This is because the nature of the excited state might be altered when the stereo-electronic features of the catalysts are altered by varying the substituents.[36] To overcome this, research from our group[33-35] has showcased the use of thioureas as a template that are amenable to systematic stereo-electronic variations to achieve high asymmetric induction during excited state transformations.

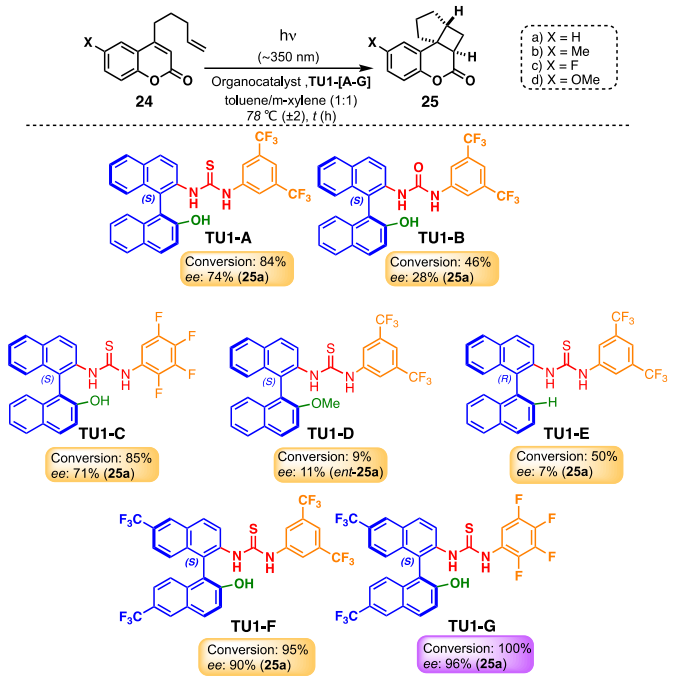
To perform a systematic evaluation of organo-photocatalyst substrate interactions and its impact on excited state reactivity, intramolecular [2+2]-photocycloaddition of 4-alkenylcoumarin **24** was evaluated with thiourea catalysts **TU1-7** leading to photoproduct **25** (Scheme 7).[34] The reason we selected thioureas as template for evaluating photoreactions is due to myriad of advantages it provides over other systems *viz.,* a) they are easy to synthesize often in few steps; b) the catalyst does not require any special handling and are stable in moisture and in aerated atmospheres; c) thioureas can be easily fine-tuned to influence their hydrogen bonding ability with electron-donating and/or electron withdrawing groups. More importantly, altering the nature of the thiourea catalysts with various substituents will not only provide us a systematic overview of how the catalyst interacts with substrates, but also how the excited state chemistry is influenced i.e., both dynamics and energetics of excited state and its impact on the photochemical reactivity of the system under investigation can be evaluated.



Scheme 7: Thiourea based hydrogen bonding motifs for enantioselective [2+2]-photocycloaddition.

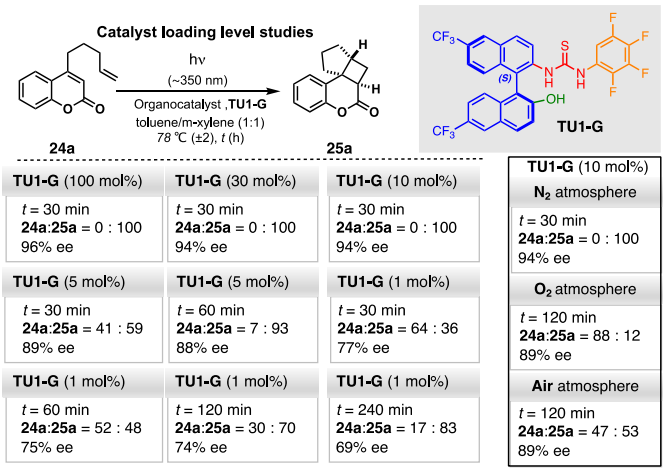
Chiral thiourea catalysts that have been successful in thermal asymmetric reactions was evaluated for intramolecular [2+2]-photocycloaddition of alkenyl-coumarin **24a** leading to the corresponding cyclized photoproduct **25a** (Scheme 7). The monofunctional Ricci's catalyst **TU6** and **TU7** gave excellent conversions of 91% and 57% respectively when compared to 9% conversions for non-catalysed reaction at similar conditions (1:1 toluene/*m*-xylene at -78 °C for 3h). Despite the high conversions, the observed photoproduct **25a** was a racemic mixture. Based on NMR titration experiments, the interaction between the coumarin substrate and the catalyst was established. The binding constant for **24e**----**TU6** interaction was ascertained to be 14.8 (±1.2) M^{-1} in $CDCl_3$. Monofunctional thiourea **TU5** gave 45% conversion with 4% *ee* in the photoproduct **25a**. The C_2-symmetrical bis-thiourea catalyst

TU3 and **TU4** gave a conversion of 72% and 84% respectively with a moderate enantiomeric excess of 24% in the photoproduct **25a**. The atropisomeric bis-thiourea catalyst **TU2** gave a conversion of 89% with 28% enantiomeric excess in **25a**. As the atropisomeric systems gave moderate enantioselectivity, NOBIN-derived thiourea catalyst **TU1** was employed for the intramolecular [2+2]-photocycloaddition of **24a** that led to 84% conversions with 74% *ee* in the corresponding photoproduct.



Scheme 8: Modulating the stereo-electronic features of NOBIN-derived thiourea catalyst for enantioselective [2+2]-photocycloaddition.

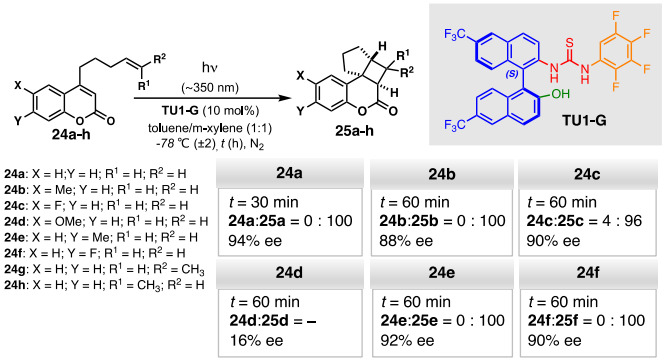
As the NOBIN-derived thiourea catalyst **TU1-A** showed promising reactivity towards enantioselective intramolecular [2+2]-photocycloaddition of **24a**, the electronic features of the thiourea catalyst were further manipulated to understand the origin of enhanced photoreactivity and stereo-differentiation mechanism (Scheme 8).[33] Enantioselective intramolecular [2+2]-photocycloaddition of **24a** with **TU1-A** was kept as a reference for evaluating other NOBIN-derived thiourea catalysts as it gave 84% conversion and 74% *ee* in 1:1 toluene/*m*-xylene at -78 °C. To understand the role of the hydrogen bonding motif, the thiourea functionality in **TU1-A** was changed to a urea functionality in **TU1-B**. Intramolecular [2+2]-photocycloaddition of **24a** with **TU1-B** gave 46% conversion with 28% enantioselectivity. The precipitous drop in both conversion and enantioselectivity showed the importance of thiourea functionality facilitating the enantioselective transformation. To understand the role of substituents on the N-phenyl ring on the thiourea, the 3,5-trifluoromethyl substituents in **TU1-A** was changed to tetrafluoro-substituted phenyl ring in **TU1-C** that resulted in a minimal change in the enantioselectivity (74% *ee* in **TU1-A** and 71% *ee* in **TU1-C**) and conversions (84% for **TU1-A** and 85% for **TU1-C**). To probe the role of binaphthyl-substituents and its impact on hydrogen-bonding ability, the hydroxyl substituent on the naphthyl ring was systematically varied (compare **TU1-A** and **TU1-D**/**TU1-E**). Replacing the hydroxyl substituent in **TU1-A** with methoxy substituent in **TU1-D** resulted in a low conversion of 9% (from 84% in **TU1-A**) with 11% enantioselectivity (from 74% *ee* with **TU1-A**). A point to note was that the optical antipode *ent*-**24a** was observed in excess with **TU1-D** when compared to **TU1-A**. Employing **TU1-E** as the catalyst that lacked hydroxyl substituent on the binaphthyl ring resulted in a conversion of 50% with low enantioselectivity of 7% in the photoproduct. Having ascertained the importance of hydrogen bonding unit appended to the bi-naphthyl ring, thioureas **TU1-F** and **TU1-G** that featured electron withdrawing CF_3 groups at the 6- and 6'-positions of the binaphthyl backbone were evaluated. Intramolecular [2+2]-photocycloaddition of **24a** with **TU1-F** led to conversions of 95% with 90% enantioselectivity in the photoproduct **25a**. Similarly, thiourea **TU1-G** gave quantitative conversions with 96% enantioselectivity the photoproduct **25a** (Scheme 8).



Scheme 9: Enantioselective [2+2]-photocycloaddition of coumarin **24a** with various loading levels of thiourea catalyst **TU1-G**.

To evaluate the impact of catalytic loading level, enantioselective [2+2]-photocycloaddition of coumarin **24a** was performed with varying amounts (1–100 mol%) of the best performing thiourea catalyst **TU1-G** (Scheme 9). Employing 10 mol% of **TU1-G** led to quantitative conversions within 30 min of irradiation with 94% enantioselectivity in photoproduct **25a**. The efficiency of asymmetric induction was also maintained in large scale reaction with 77% isolated yield and 92% enantioselectivity in the product. Decreasing the loading level of the catalyst below 10 mol% led to a slight decrease in the enantiomeric excess which was rationalized due to the competing background reactions at low loading levels.

The generality of enantioselective photocycloaddition catalyzed by thiourea **TU1-G** (10 mol%) was evaluated with coumarin derivatives **24a-f** (Scheme 10). Varying the substituent at the 6-position of coumarin to electronic rich methyl group (e.g., **24b**) and electron deficient fluorine substituent (e.g., **24c**) resulted in 88% and 90%



Scheme 10: Substrate scope for enantioselective [2+2]-photocycloaddition of coumarin derivatives with thiourea catalyst **TU1-G.**

enantioselectivity in the corresponding photoproduct. There was a significant drop in the enantioselectivity to 16% when methoxy coumarin **24d** was employed for [2+2]-photocycloaddition. This revealed that the hydrogen-bonding interactions between the thiourea catalyst and the substrate was disturbed by the 6-methoxy substituent in **24d**. Thiourea catalyst **TU1-G** (10 mol %) was also effective for enantioselective [2+2]-photocycloaddition of 7-substituted coumarins **24e** and **24f** leading to enantioselectivity of 92% and 90%, respectively. The reaction atmosphere had a profound impact on the reaction efficiency but the enantioselectivity was not significantly affected (Scheme 9). Photoreaction of **24a** with 10 mol% of **TU1-G** under nitrogen, oxygen and aerated conditions gave quantitative, 12% and 53% conversions, respectively. In spite of the variation in conversion the enantioselectivity was not affected significantly, that showed a reactive triplet diradical intermediate int-**24** (Scheme 7). This was further confirmed by employing internal alkenes **24g** and **24h** (Scheme 10) with thioureas **TU1-A** that showed scrambling of the alkene geometry i.e, *cis*/*trans* isomerization of the alkene double bond was observed in addition to the photocycloaddition reaction. These once again pointed to the involvement of a triplet 1,4-biradical int-**24** (Scheme 7) during the catalytic process.

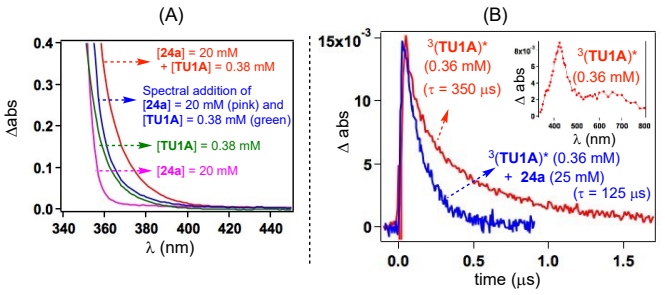


Figure 2: Photophysical investigations for ascertaining catalyst-substrate interactions. (A) UV/Vis absorption spectra in methylcyclohexane (MCH). (B) Transient absorption decay traces of ^{3}(**TU1-A**)* monitored at 425 nm after pulsed laser excitation (355 nm, 5 ns) and transient absorption spectrum of **TU1-A** in deoxygenated MCH (inset). Reproduced with permission from reference 33. Copyright 2014 John Wiley and Sons

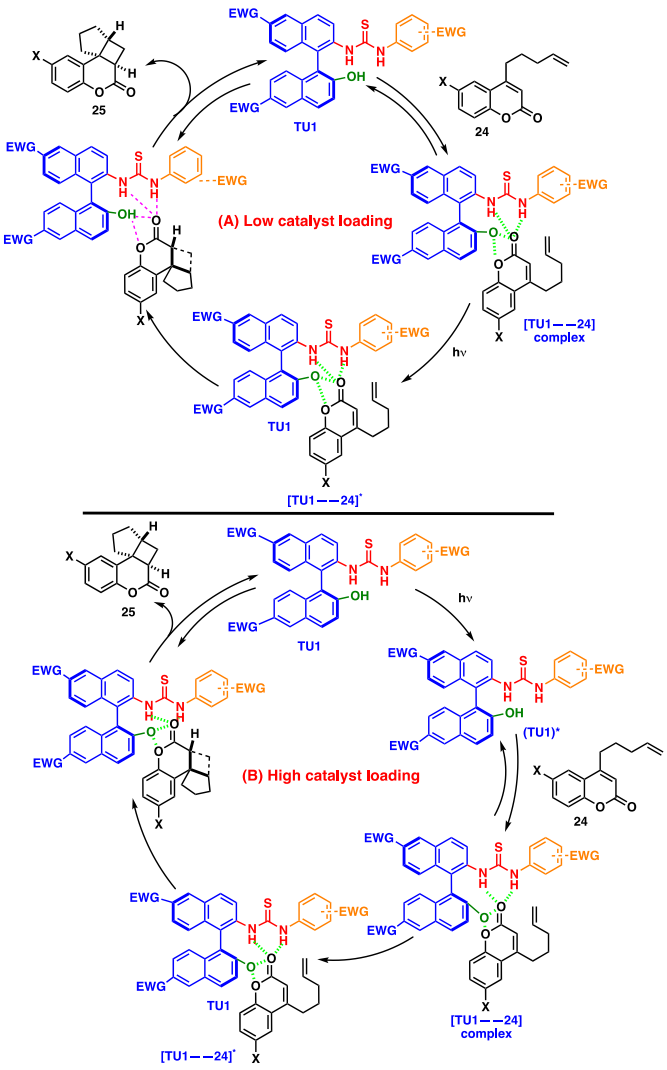
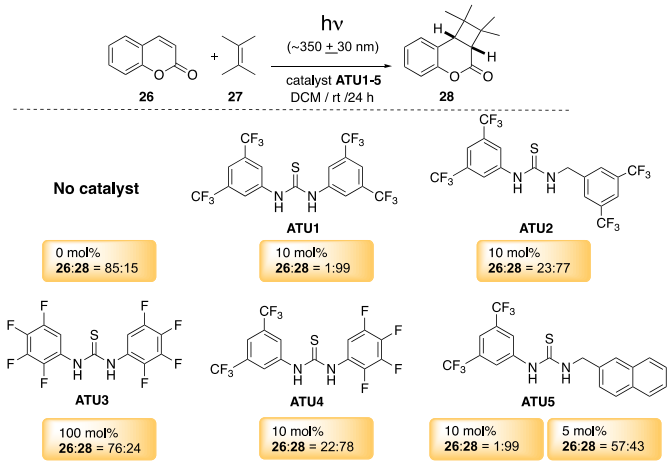


Figure 3: Mechanistic features of thiourea mediated enantioselective organo-photocatalysis at low (top) and high (bottom) catalytic loading levels. Adapted from reference 33. Copyright 2014 John Wiley and Sons

The role of **TU1-A** catalyst in promoting the photoreaction was investigated by performing extensive photophysical studies. The absorption spectra of the substrate shifted bathochromically (Figure 2A) in the presence of the thiourea catalyst. Even though, the excited state energy of the substrate **24a** (excited singlet-state E_S=84 kcal/mol and excited triplet-state E_T=64 kcal/mol) was higher than the thiourea catalyst **TU1-A** (excited singlet-state E_S=77 kcal/mol and excited triplet-state E_T=58 kcal/mol) the photoproduct was generated efficiently during the photoreaction. There was also efficient quenching of the **TU1-A** excited state by coumarin substrate **24a**. Transient absorption measurements showed a dynamic complex between catalyst and the reactant (Figure 2B). This led to the suggestions of a dual catalytic cycle depending on the loading level of the catalyst and the hydrogen-bonding interactions between **TU1-A** and coumarin substrate (Figure 3). The light absorbing species was likely determined by the catalyst loading level (Figure 2A). At low catalyst loading levels,

the catalyst–substrate complex had a bathochromic shift in the absorption spectrum. This catalyst–substrate complex upon photoexcitation reacted efficiently to form the product via a triplet 1,4-diradical (Figure 3-top). At high catalyst loading levels (Figure 3-bottom), the thiourea catalyst was excited due to its higher absorptivity. The catalyst excited state was quenched effectively by the substrate in spite of the excited state energy mismatch as they proceed through an exciplex. This exciplex reacted effectively to form the photoproduct through a triplet 1,4-diradical intermediate.

Our group also extended the strategy of employing thioureas for catalysing intermolecular [2+2]-photochemical reactions of coumarin **26** with alkene **27** leading to photoproduct **28** (Scheme 11).[35] In the absence of any thiourea catalyst the reaction was inefficient with <4% conversion. However, in the presence of the achiral thiourea **ATU1-5** the conversion ranged from 22-76% with the naphthyl substituted achiral thiourea **ATU5** being the most effective for the intermolecular photocycloaddition (Scheme 11). The photocycloaddition reaction with 10 and 5 mol% of **ATU5** gave a reactant to product ratio (**26**:**28**) of 1:99 and 57:43, respectively (Scheme 11). The achiral thiourea **ATU4** was found to interact with both the reactant **26** and the photoproduct **28** with association constant (K_a) of 6.3 M^{-1} and 4.8 M^{-1}, respectively.



Scheme 11: Achiral thiourea (**ATU**) as organo-photocatalyst for intermolecular [2+2]-photochemical reaction of coumarin **26** with tetramethyl ethylene **27**.

Photophysical investigations revelated that there was no bathochromic shift in coumarin absorption in the presence of achiral thioureas **ATU**s (Scheme 11) which was quite different from what was observed with NOBIN-derived thioureas **TU**s (Schemes 7). There was no appreciable fluorescence from **26** in toluene at room temperature while strong fluorescence centred around 408 nm and weak phosphorescence (overlapping with the fluorescence signal) was observed at 77K in methylcyclohexane (MCH) glass. Kinetic decay analysis of the luminescence at 412 nm showed two lifetimes of 1.2 ns and 4.0 ns. It was conjectured that the emission characteristics are due to monomer and the dimeric aggregate of **26** in MCH glass at 77K. Luminescence measurements with a 1:1 mixture of catalyst **ATU4** and **26** displayed a reduction in the coumarin fluorescenc as well as its corresponding lifetimes at 412 nm (i.e., 0.6 ns and 3.2 ns). In addition, the emission intensity of the 1:1 mixture of **ATU4** and **26** depended on the excitation wavelength (compare Figures 4A and 4B). Excitation at 340 nm displayed weak emission from the coumarin and a new emission centred at approximately 523nm was observed, while excitation at 360 nm where coumarin **26** does not have any absorption

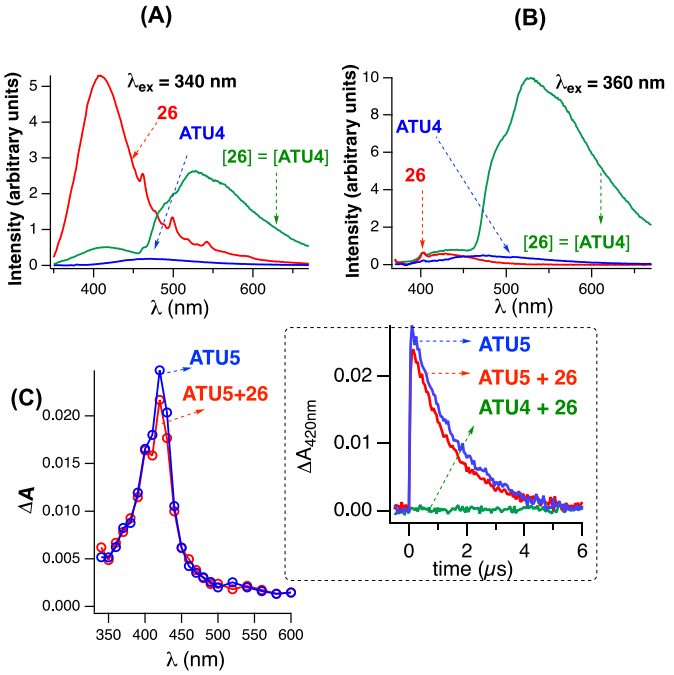


Figure 4: Photophysical investigations for deciphering the role of achiral thioureas in promoting intermolecular [2+2]-photocycloaddition. (Top) Steady-state luminescence spectra with λ_{ex}=360 nm (A) and λ_{ex}=360 nm(B). (Bottom) Transient absorption spectra recorded 0–0.4 μs after pulsed laser excitation (λ_{ex} =355 nm, 5 ns pulse width) of argon-saturated toluene solutions of **ATU5** (2 mM) in the absence (blue) and presence (red) of **26** (2 mM). Inset: Absorbance kinetic traces monitored at 420 nm. Reproduced with permission from Reference 35. Copyright 2014 John Wiley and Sons.

displayed predominantly the new emission band centred around 523 nm. This emission was rationalized due to the selective excitation of coumarin–catalyst complex. The properties of the triplet states of coumarin and achiral thiourea **ATU5** were investigated by phosphorescence spectroscopy in a toluene matrix at 77 K that revealed a ππ* configuration in both the catalyst and the reactant. Pulsed laser excitation of a 1:1 mixture of **26** (2 mM) and achiral thiourea **ATU5** at 355nm generated a transient absorption spectrum with a maximum at 420 nm (Figure 4C, red spectrum), which decayed monoexponentially with a lifetime of 1.5 μs (Figure 4C). Similar transient absorption spectrum was observed in the absence of **26** indicating that it has its origin from the excited catalyst. This transient absorption generated from **ATU5** was not quenched by the coumarin **26** as well as by **27** even at a high concentration

indicating the naphthalene triplet in **ATU5** was not involved in enhancing the rate of the reaction. Based on these studies a mechanistic model was proposed (Figure 5) in which the enhanced intermolecular [2+2]-photocycloaddition of **26** in the presence of achiral thioureas was due to the minimized aggregation of coumarin **26**(based on luminescence studies in MCH, Figures 4A and 4B). In addition, the phosphoresce showed an enhanced intersystem crossing (ISC) in coumarin, that was reflected in the enhancement of the phosphorescence signal along with altered excited-state lifetimes. The change in the above excited-state properties was initiated by hydrogen bonding interaction between the reactant and the thiourea catalyst. Thus, the investigation revealed the function of thiourea catalyst in both intramolecular [2+2]-photocycloaddition (Schemes 6-9) and intermolecular [2+2]-photocycloaddition (Scheme 11).

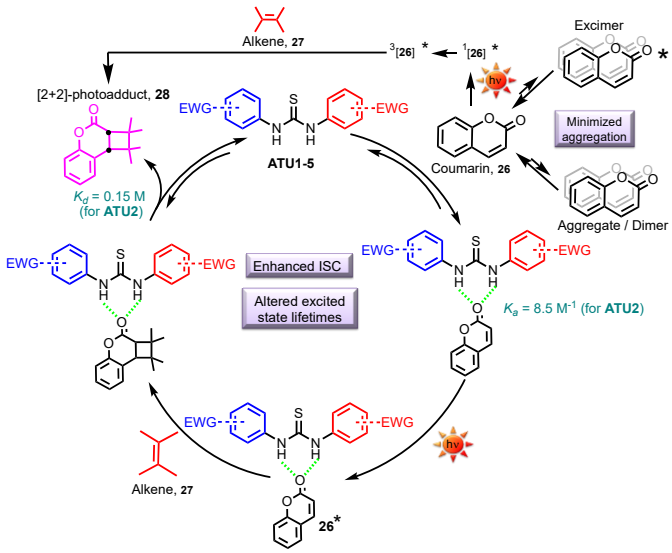


Figure 5: Mechanistic details for organo-photocatalytic intermolecular [2+2]-photochemical reaction of coumarin **26** with tetramethylethylene **27**. Adapted with permission from Reference 35. Copyright 2014 John Wiley and Sons.

Future outlook on BrØnsted acids for controlling excited state asymmetric

One of the critical aspects that researchers need to consider when designing organo-catalysts in general for excited state transformations is how the substitution will affect the energy and dynamics of the excited state. [33-35] This requires an in-depth study of photophysical features in addition to evaluating the photochemical aspects.[33-35] Combining the knowledge gained from both photochemistry and photophysical measurements new and exciting aspects related to excited state asymmetric photochemical reactions can be evaluated in depth to enhance its utility and scope.

Conclusions

The rich chemistry of hydrogen bonding mediated photochemical transformations has certainly evolved from reactions in crystalline media to asymmetric phototransformations from solution. Since our report on utilizing thioureas as organo-photocatalyst, multiple groups have utilized thiourea derived catalysts for controlling photochemical reactions.[37, 38] Recently, BrØnsted acids derived from phosphoramide has shown potential in intermolecular asymmetric [2+2]-photocycloaddition reaction.[39] These developments are certain to pave a way for a bright and fruitful evaluation of BrØnsted acids mediated organo-photocatalysis.[40]

Author Contributions

The Feature article was written by all the co-authors under the guidance of JS.

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Conflicts of interest

The authors declare no conflicts.

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Prof. Dr. Jayaraman Sivaguru (Siva) is the Antonia and Marshall Wilson Professor of Chemistry and the Associate Director for the Center for Photochemical Sciences at the Department of Chemistry, Bowling Green State University, Bowling Green, Ohio. Prof. Sivaguru is well known for his contributions to the area of photochemical sciences. He has been recognized with numerous awards over the last decade. In 2021, Prof. Sivaguru was the recipient of the Honda-Fujishima Lectureship award from the Japanese photochemical association. His research program studies both the fundamental and applied aspects of photochemistry.

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