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Organophotocatalysis: Insights into the Mechanistic Aspects of Thiourea-Mediated Intermolecular [2 + 2] Photocycloadditions

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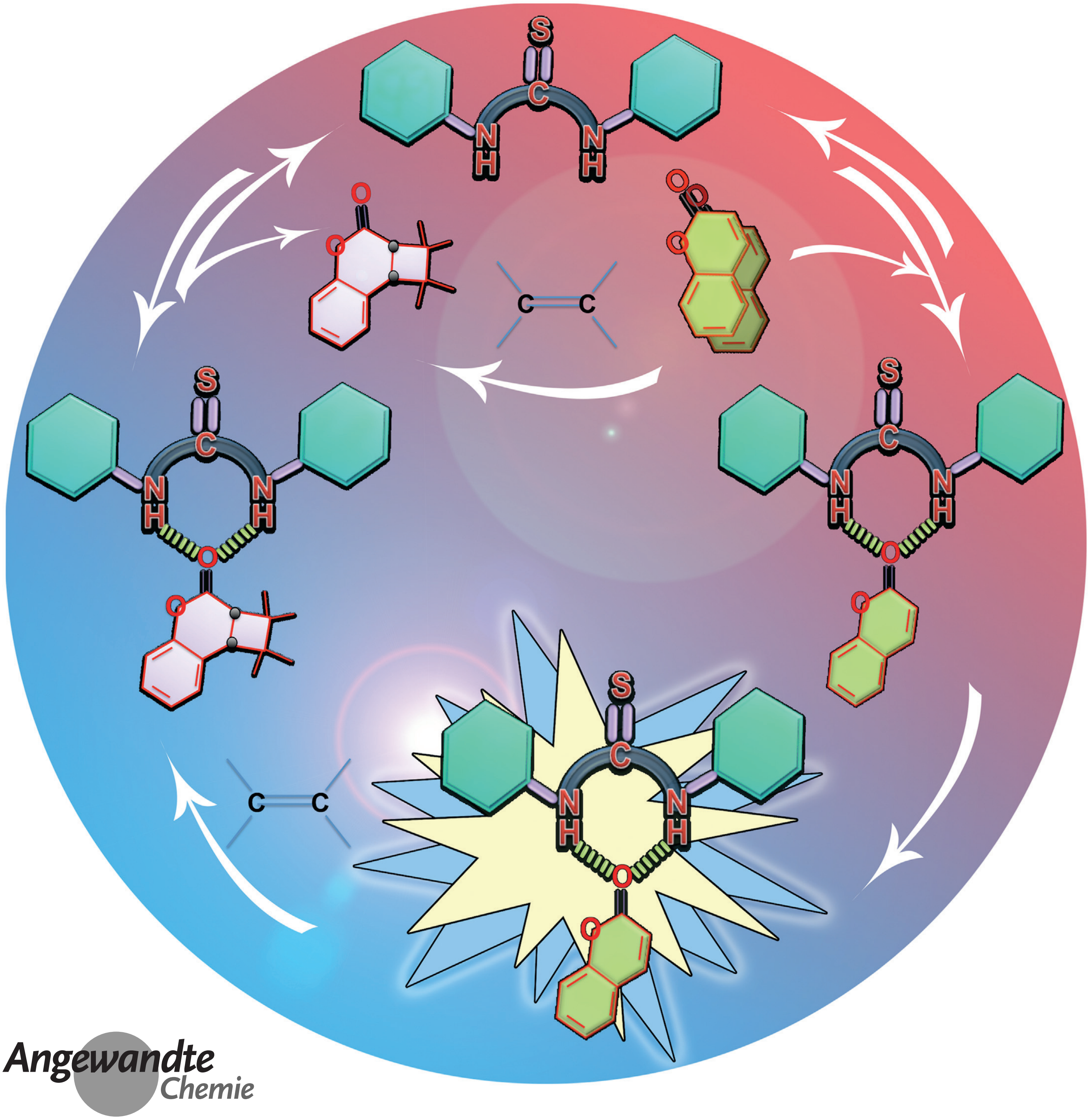

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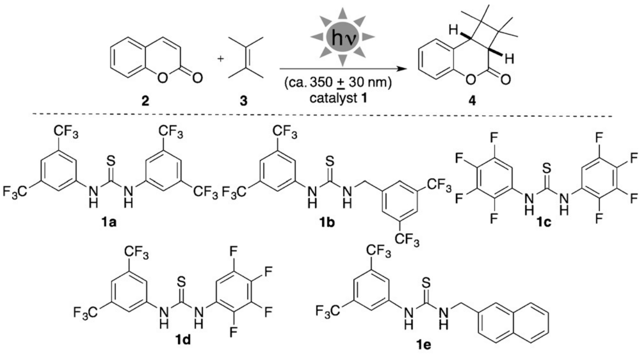
Abstract: *Mechanistic investigations of the intermolecular [2+2] photocycloaddition of coumarin with tetramethylethylene mediated by thiourea catalysts reveal that the reaction is enabled by a combination of minimized aggregation, enhanced intersystem crossing, and altered excited-state lifetime(s). These results clarify how the excited-state reactivity can be manipulated through catalyst–substrate interactions and reveal a third mechanistic pathway for thiourea-mediated organo-photocatalysis.*

Catalytic transformations play a central role in chemical and biological processes.[1] Environmentally benign catalytic processes must not only be attractive from an ecological perspective but also be sustainable. Organo-photocatalytic transformations[2] based on supramolecular interactions have rightfully attracted attention owing to their promise in initiating and propagating catalytic processes by employing light as the energy source in combination with organic templates. Recently, several groups[2] have cleverly exploited photoredox catalysts with a high degree of versatility for various chemical transformations. Controlling the photochemistry and photophysics of organic chromophores in solution to achieve selective photochemical transformations has been a challenge owing to the short lifetimes of the reactive excited states.[3] Supramolecular scaffolds have been employed effectively to control the excited-state processes with high efficiency.[3] Compared to thermal reactions, carrying out photochemical transformations with a high degree of selectivity during large-scale laboratory synthesis has presented formidable obstacles. Whereas catalyzing photochemical transformations with Lewis acids or hydrogen-bonding activators is attractive, a mechanistic understanding of these processes provides an avenue to generalize the overall methodology.[2b,4] Recently, we reported that organocatalysts based on atropisomeric thiourea derivatives are superior templates for mediating enantioselective photoreactions, and proposed a novel mechanism that proceeded by energy sharing mediated through hydrogen-bonding interactions.[5] We established that two distinct reaction pathways are feasible depending on the loading of the thiourea catalyst.[5a] To determine whether the same mechanistic rationale is applicable to intermolecular reactions, we evaluated thiourea[1b,6] and urea derivatives as catalysts for the [2+2] photocycloaddition of coumarin (**2**) with tetramethylethylene (**3**).[7] Herein, we report a third mechanistic pathway where thiourea catalysts influence the excited-state reactivity through a combination of minimized aggregation, enhanced intersystem crossing, and altered excited state lifetime(s).

The intermolecular [2+2] photocycloaddition of coumarins[7,8] with alkenes in solution is an inefficient process. This is due to the nature of the excited coumarin chromophores, which decay both radiatively (emission) and non-radiatively (internal conversion) from the excited state to the ground state. Nevertheless, the photochemical reactivity of coumarins could be modulated by 1) confinement within supramolecular assemblies/templates that restrict molecular motion[9] and by 2) complexation to Lewis acids that interact with the carbonyl moiety, thereby altering the nature of the excited state.[4d,8a,c,d] As intermolecular photoreactions are often challenging owing to the dynamics involved in the excited state, catalysts that impact photochemical reactivity are likely to not only affect the rates of the photoreaction but also alter the rates of other excited-state processes. We employed thioureas **1a**–**1e** (Scheme 1)[1b,6,10] and urea derivatives **1f**–**1h** (Supporting Information, Chart S1)[11] as efficient photocatalysts for the intermolecular [2+2] cycloaddition of coumarin (**2**) with tetramethylethylene (**3**) as we envisioned that coumarin aggregation and excited-state deactivation/lifetimes influence its reactivity.[7]



Scheme 1. Intermolecular [2+2] photocycloaddition of coumarin (**2**) with tetramethylethylene (**3**) with thiourea organocatalysts **1a**–**1e**.

To evaluate the viability of employing thioureas **1a**–**1e** and urea derivatives **1f**–**1h**[11] as photocatalysts, we selected the symmetric thiourea catalysts **1a** and **1c** (compounds with the same aryl units on either side of the thiourea functional group) and the unsymmetric catalysts **1b**, **1d**, and **1e** (compounds with different aryl units on either side of the thiourea functional group).[1b,10a–e] To compare the efficiencies of the thiourea catalysts with those of the corresponding urea catalysts, we synthesized the symmetric urea catalyst **1f** (i.e., the urea analogue of **1a**) and the unsymmetric urea catalysts **1g** and **1h**, which are the urea analogues of **1b** and **1d**, respectively.[11] To assess their effectiveness in promoting the photocycloaddition of **2** with **3** (10 equiv), 100 mol% of **1a**–**1h** were employed in combination with 350 ± 30 nm irradiation in a Rayonet reactor for 19 h (Table 1).[11] As a control, the reaction was carried out in the absence of catalyst and compared with previously reported results (4% conversion for 68 h irradiation of **2** with 10–20 equiv of **3** with > 310 nm

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Table 1: Catalyst screening for the [2+2] photocycloaddition of **3** and **2** in CH_2Cl_2.[a]

Entry	Catalyst	**2**/**4**[b]	MB[c] [%]	Conv.[c] [%]	Yield[c] [%]
1	–	89:11	86	11	9
2	**1a**	32:68	96	65	62
3	**1b**	38:62	96	56	54
4	**1c**	76:24	88	22	19
5	**1d**	38:62	93	58	54
6	**1e**	22:78	96	76	73

[a] Catalyst loading: 100 mol%; irradiation time: 19 h. Averages of a minimum of three runs (error: ±5%) are given. [b] Determined by GC analysis with a ChirasilDex-CB column. [c] The conversion of **2**, the mass balance (MB), and the yield of **4** were determined by ^1H NMR spectroscopy using triphenylmethane as an internal standard in $CDCl_3$ or CD_3CN.

Table 2: Influence of the catalyst loading on the intermolecular [2+2] photocycloaddition of **3** and **2** in CH_2Cl_2 for various thiourea catalysts.[a]

Entry	Catalyst (mol%)	**2**/**4**[b] 12 h	24 h	36 h	40 h
1	–	95:05	85:15	77:23	66:34[c]
2	**1a** (10)	23:77	01:99	–[d]	–[d]
3	**1b** (10)	56:44	23:77	10:90	7:93
4	**1d** (10)	55:45	22:78	10:90	–[d]
5	**1e** (10)	31:69	01:99	–[d]	–[d]
6	**1e** (5)	75:25	57:43	46:54	31:69[d]
7	**1e** (1)	87:13	77:23	65:35	50:50[d]

[a] Averages of a minimum of three runs are given (error: ±5%). [b] Determined by GC analysis with a ChirasilDex-CB column. [c] Irradiated for 48 h. [d] >90% conversion observed with shorter irradiation times. Hence, longer irradiation times were not studied. For further studies on the catalyst loading, see the Supporting Information.

transmission using a 450 W medium-pressure mercury lamp).[7]

Table 1 reveals that the thiourea-based organocatalysts are effective in promoting the [2+2] photocycloaddition of coumarin with tetramethylethylene with moderate to high conversion and with excellent mass balance. The conversion was higher with the thiourea than with the corresponding urea catalyst.[11] For example, 65% conversion was observed with thiourea **1a** compared to 30% conversion with the corresponding urea **1f**.[11] Other symmetric and unsymmetric catalysts gave modest conversions (Table 1; see also the Supporting Information, Table S1).[11] The most striking result was achieved with the naphthyl-substituted catalyst **1e**, which gave 76% conversion with excellent (96%) mass balance (Table 1, entry 6). As thiourea-based catalysts were effective in promoting the intermolecular photoreaction of **2** with **3**, it became critical to ascertain the best solvent(s) for this photocatalytic process. We investigated the efficiency of the photocycloaddition using **1a**, **1b**, **1d,** and **1e** in four different solvents, namely methylcyclohexane (MCH), toluene, tetrahydrofuran (THF), and dichloromethane.[11] In dichloromethane and toluene, the reaction proceeded with excellent conversion, yield, and mass balance (Table S2).[11] In THF, the conversion varied between 26 to 99%, and the mass balance was moderate.[11] Low conversions and product yields were observed in MCH.

Based on the results shown in Table S2, we selected dichloromethane as the solvent of choice to investigate the efficiency of the reaction with respect to the thiourea catalyst loading (Table 2). The catalyst loading was varied from 70 mol% to 10 mol% for thioureas **1a**, **1b**, and **1d** (Table S3, entries 2–13)[11] and from 70 mol% to 1 mol% in the case of **1e** (Table S3, entries 14–19).[11] To compare the efficiency of the thioureas at different loadings, the reactant/photoproduct ratio (**2**/**4**) was investigated at various irradiation times (12–48 h) for a given amount of catalyst. Table 2 shows that at a catalyst loading of 10 mol%, the **2**/**4** ratio for 24 h irradiation was 1:99 for **1a** (entry 2), 23:77 for **1b** (entry 3), 22:78 for **1d** (entry 4), and 1:99 for **1e** (entry 5). As catalyst **1e** was found to be optimal for the [2+2] photocycloaddition of **2** with **3**, we investigated its efficiency at loadings of 5 and 1 mol%. With 5 mol% of **1e**, the **2**/**4** ratio was 31:69 (entry 6), and at 1 mol% loading, the ratio of **2**/**4** was 50:50 (entry 7) after 40 h irradiation. As expected, longer irradiation times were required for lower catalyst loadings to achieve a similar level of conversion. Evidently, the thiourea catalyst **1e** efficiently facilitated the reaction with good turnover even at low catalyst loading. To demonstrate the versatility of the thiourea catalyst in promoting large-scale photoreactions, we performed the reaction on gram scale. We achieved 80% conversion with 30 mol% of **1b**, and the desired photoproduct was isolated in 75% yield.[11]

Detailed photophysical investigations were carried out to understand the role of the thiourea catalysts in promoting the [2+2] photocycloaddition of **2** with **3**. Thioureas **1d** and **1e** were selected to understand the role of both the thiourea and naphthalene chromophores in promoting the photoreaction. Absorption spectra of the thioureas and **2** were recorded to determine which of the chromophores is predominantly absorbing light. Coumarin shows no absorbance above 350 nm, whereas **1d** absorbs weakly up to 400 nm (Figure 1A). It should be pointed out that the 350 nm lamp that was used for the photocatalytic reactions has a spectral width of ± 30 nm. No appreciable fluorescence was observed for **2** at room temperature in toluene. We thus recorded the luminescence of **2** at 77 K in MCH glass (Figures 1B). We observed strong fluorescence centered around 408 nm and weak phosphorescence (overlapping with the fluorescence signal).[11] The emission characteristics matched the previously reported profile,[12] which was rationalized to be due to the monomer and the dimeric aggregate of **2** in MCH glass at 77 K. Kinetic decay analysis of the luminescence at 412 nm showed two lifetimes of 1.2 ns and 4.0 ns.[11] On the other hand, luminescence measurements with a 1:1 mixture of **1f** and **2** showed a significant reduction of the coumarin fluorescence in addition to reduced lifetimes at 412 nm (0.6 ns and 3.2 ns).[11] More importantly, for a 1:1 mixture of **2** and **1d**, the emission intensity depended on the excitation wavelength (Figure 1B,C). For the 1:1 mixture of **2** and **1d**, with $\lambda_{ex} = 340$ nm, weak emission from the coumarin and a new emission centered at approximately 523 nm were observed. Upon changing the excitation wavelength to 360 nm, where **2** does not have any significant absorption, the new emission band was predominantly observed, which is likely due to the selective excitation of the coumarin–catalyst

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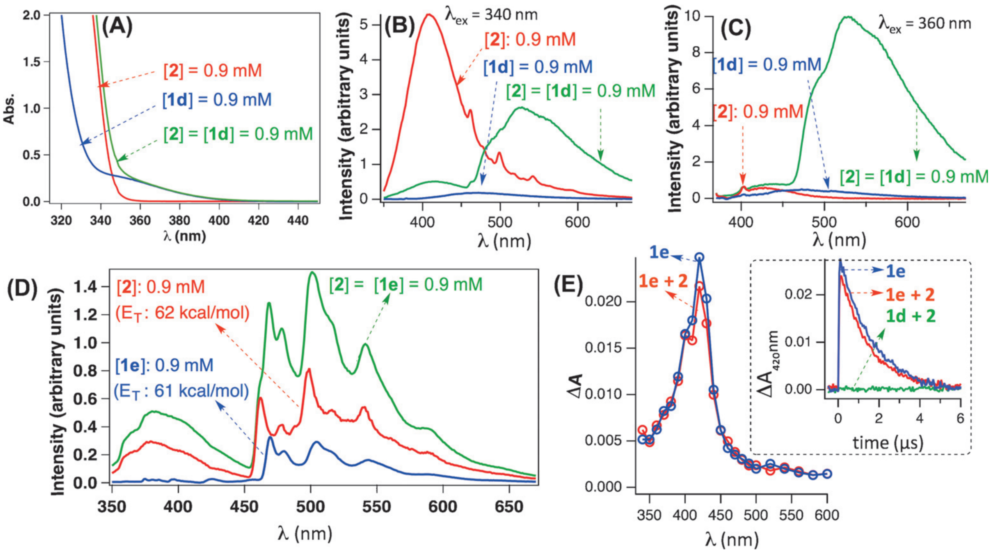

Figure 1. A) Absorption spectra of **1d**, **2**, and a 1:1 mixture of **1d** and **2** in toluene. B, C) Steady-state luminescence spectra of **1d**, **2**, and a 1:1 mixture of **1f** and **2** in MCH glass at 77 K at $\lambda_{ex} = 340$ nm (B) and $\lambda_{ex} = 360$ nm (C). D) Steady-state luminescence spectra of **1e**, **2**, and a 1:1 mixture of **1e** and **2** in toluene glass at 77 K. E) Transient absorption spectra recorded 0–0.4 μs after pulsed laser excitation ($\lambda_{ex} = 355$ nm, 5 ns pulse width) of argon-saturated toluene solutions of **1e** (2 mM) in the absence (blue) and presence (red) of **2** (2 mM). Inset: Absorbance kinetic traces monitored at 420 nm of **1e** (2 mM; blue), **1e** and **2** (red), and **1d** and **2** (green).

complex (Figure S20).[11] Based on time-resolved luminescence studies, this emission was found to originate from the triplet excited state. The properties of the triplet states of coumarin and catalyst **1e** were investigated by phosphorescence spectroscopy in a toluene matrix at 77 K (Figure 1 D). The triplet energy of **2** (62 kcal mol^{-1}) was determined from the first peak of the phosphorescence spectrum with a lifetime (τ_p) of 0.3–0.5 s.[11] The phosphorescence of catalyst **1e** is slightly red-shifted compared to that of coumarin, which shows that **1e** has a slightly lower triplet energy (61 kcal mol^{-1}). The phosphorescence lifetime of catalyst **1e** in toluene glass at 77 K was 1.1 s.[11] Based on the phosphorescence lifetimes, it is clear that the lowest triplet excited states of both catalyst **1e** and substrate **2** have ππ* configuration.

Laser flash photolysis was performed to investigate the reactivity of the triplet states (Figure 1 E). Pulsed laser excitation of a 1:1 mixture of **2** (2 mM) and catalyst **1e** at 355 nm generated a transient absorption spectrum with a maximum at $\lambda = 420$ nm (Figure 1 E, red spectrum), which decayed monoexponentially with a lifetime of 1.5 μs. In the absence of **2**, a similar transient absorption spectrum was observed (blue spectrum). Consistent with literature reports for other naphthalene derivatives that also show transient absorbance around 420 nm,[13] this transient absorption spectrum was assigned to the triplet–triplet absorption of **1e**. Furthermore, pulsed laser excitation of a mixture of **2** and **1d**, a catalyst that does not contain a naphthalene substituent, did not show transient absorption (Figure 1 E, inset, green line). The transient absorption generated from **1e** was quenched neither by **2** (Figure 1 E, inset, red line) nor by tetramethylethylene (Figure S17),[11] even at a high concentration of 50 mM, suggesting that the naphthalene triplet excited states of **1e** are not directly involved in the [2+2] cycloaddition. This finding implies that the thiourea unit is likely to be responsible for the enhanced reactivity. The bimolecular rate constant for the [2+2] photocycloaddition of the coumarin triplet states with tetramethylethylene was determined by laser flash photolysis.[11] Pulsed laser excitation of **2** at 308 nm gave a weak transient absorption centered around 400 nm, which had previously been assigned to the triplet state of the coumarin chromophore.[14] Decay traces at different concentrations of **3** were recorded and fitted to a first-order decay function. The bimolecular rate constant ($k_q \approx 2 \times 10^8\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) was obtained from the slope of the plot of the inverse triplet lifetime versus the concentration of **3**.[11]

A few solid-state structures of catalysts bound to substrates have been reported in the literature on photoreactions.[20] Herein, we provide a crystal structure of catalyst **1f** bound to substrate **2** (Figure 2) to highlight the catalyst–substrate interactions.[21] Inspection of the single-crystal XRD structure revealed an NH⋯O=C distance of approximately 2.05 Å and an N⋯O=C distance of about 2.87 Å, indicating weak-to-moderate hydrogen-bonding interactions between the catalyst and the substrate (Figure 2).[15] As the hydrogen-bonding interactions had been ascertained in the crystalline state, it became critical to evaluate the magnitude of the interaction that existed between the catalyst and the substrate in solution to comprehend its effect on photocatalysis. To address this aspect, thermodynamic binding analysis of both substrate **2** and photoproduct **4** was performed with thioureas **1a**, **1b**, and **1d** (Table S10).[11,16] Both substrate **2** and photoproduct **4** were bound to the thiourea catalysts, with the association constants for the coumarin being slightly higher than for photoproduct **4**. For example, in the case of

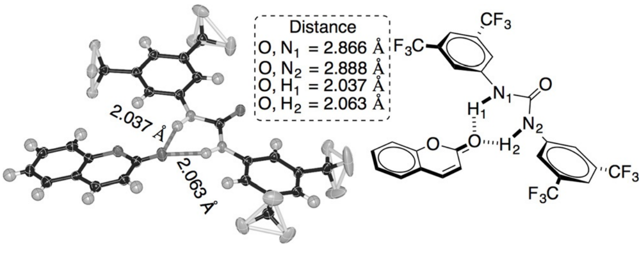

Figure 2. Single-crystal XRD of catalyst **1f** with coumarin (**2**).

1d, the association constant (K_a) for coumarin was $6.3\,\text{M}^{-1}$, and the corresponding dissociation constant (K_d) for the photoproduct **4** was $0.21\,\text{M}$ ($K_a = 4.8\,\text{M}^{-1}$).[11]

We suggest that the rate enhancement observed for the photoreaction using urea and thiourea catalysts is due to the hydrogen bonding between the NH units of the catalysts and the carbonyl group of the coumarin, with the [2+2] photocycloaddition probably occurring from the triplet state of **2**.[17] Having ruled out the involvement of the naphthalene triplet excited state of catalyst **1e** in promoting the photoreaction of **2** with **3**, the question that needs to be addressed is how the thiourea catalyst promotes the photoreaction. We suggest that upon complexation of the thiourea catalyst with coumarin, both its ground-state and excited-state properties are affected. This is reflected in 1) the minimized aggregation of coumarin (based on luminescence studies in MCH, Figure 1B), 2) the enhanced intersystem crossing (ISC) in coumarin (reflected in the phosphorescence signal enhancement, Figure 1D), and 3) altered excited-state lifetimes (derived from luminescence kinetic decay analysis).[11] Altering excited-state properties by non-covalent interactions is well established in the literature,[18] and in the present case, we have exploited this effect for promoting the efficiency of the intermolecular [2+2] photocycloaddition of coumarin with an alkene using catalytic amounts of a thiourea catalyst.

Based on our observations, we propose a likely photocatalytic cycle (Figure 3) in which the thiourea/urea catalyst binds coumarin through hydrogen bonding. Upon light excitation of coumarin **2**, the triplet yield and lifetime are altered owing to interactions with the thiourea catalysts. This enables **2** to react efficiently with alkene **3** to form photoproduct **4**. Whereas intramolecular photocycloadditions involving coumarins proceed by two mechanistic pathways depending on the amount of the thiourea catalyst (via an exciplex or a ground-state complex), the intermolecular [2+2] photocycloaddition of coumarins mediated by thioureas involves minimized aggregation, enhanced intersystem crossing, and altered excited-state lifetime(s).

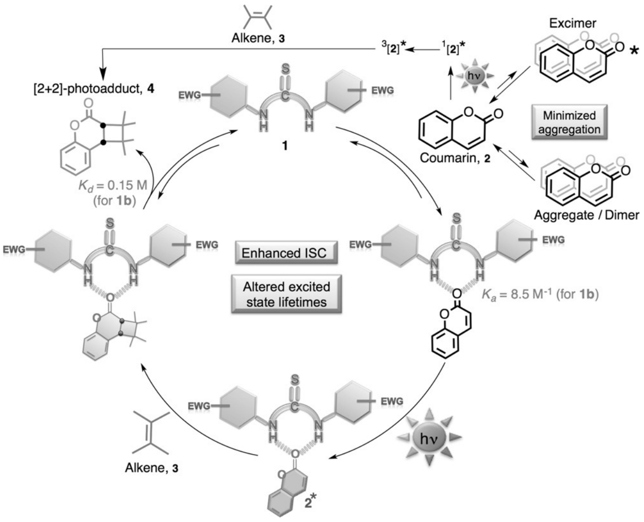

Figure 3. Proposed organo-photocatalytic cycle mediated by thioureas.

Our current study has showcased the influence of thioureas (and ureas) as catalysts to promote intermolecular photochemical reactions. As urea and thiourea catalysts with various functionalities are easily synthesized and readily fine-tuned (in terms of their electronic and steric properties), they can easily be utilized to influence photocatalytic processes. We have also demonstrated that both the photochemistry and the photophysics of individual systems need to be investigated to provide insights into the mechanism of substrate activation during the photoreaction.[19]

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Keywords: asymmetric catalysis · organocatalysis · photochemistry · photocycloadditions · thioureas

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[21] CCDC 1457146, 1457147, and 1457148 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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