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Application of PET deprotection for orthogonal photocontrol of aqueous solution viscosity†

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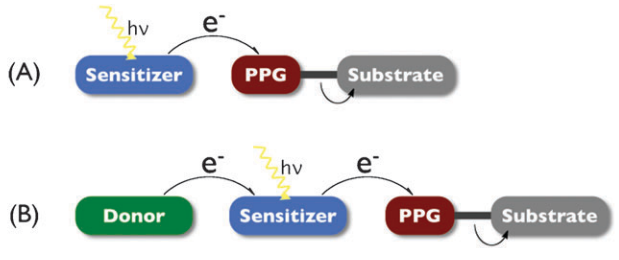
Photorelease and photoisomerization of *trans*-cinnamic acid in aqueous CTAB solutions induces a bulk solution viscosity increase and decrease, respectively, triggered by orthogonal irradiation wavelengths.

Photorelease of functional molecules has found broad utility in materials and biological sciences. Photolabile protecting groups (PPGs) are frequently the active component in these systems and have been developed for lithographic applications[1,2] as well as the release of "caged" biologically significant compounds (*e.g.*, caged ATP, glutamate, *etc.*).[3,4] Commonly studied PPGs include derivatives of the nitrobenzyl, benzoin, phenacyl, and coumarin families.[5,6] Our efforts have focused on utilizing sensitized photoinduced electron transfer (PET) to release a PPG that responds to one electron reduction[7] (Scheme 1A). The *N*-alkylpicolinium (NAP) group has been the primary PPG that we have used to protect carboxylates, phosphates, and amino acids.[8–10] Release of protected substrates using sensitizers absorbing UV or visible light irradiation has been demonstrated. Furthermore, we have developed several aqueous compatible systems utilizing a large excess of an inexpensive electron donor along with a sub-stoichiometric amount of visible light absorbing sensitizers (mediated deprotection, Scheme 1B).[8,11,12] An electron is shuttled between the donor and the NAP group by the sensitizer (mediator) to release the substrate in these systems.

Having developed these useful systems, we sought to demonstrate their applicability to produce higher order responses upon photolysis. Our interest was drawn toward systems developed to modulate solution viscosity through the photoisomerization of *trans ortho*-methoxycinnamic acid (OMCA) in aqueous solutions of the cationic surfactant cetyl trimethylammonium bromide (CTAB).[13] Aqueous solutions of CTAB are well known to form wormlike micelles upon addition of certain aromatic carboxylates and sulfonates.[14–16] In the presence of *trans*-OMCA, CTAB forms long, entangled wormlike micelles, resulting in very high solution viscosities. Upon UV-induced *trans* to *cis* photoisomerization, the geometry of OMCA is altered,[17] and in turn, the *cis*-OMCA molecules tend to desorb from the micelles. This leads to shorter micelles and thus to lower solution viscosities. A key goal in the development of these photorheological (PR) fluids[18] is to achieve a high degree of viscosity reversibility for applications such as microfluidic flow-control valves.[19–21] While, in principle, it should be possible to reverse the above changes, the similarities in absorption properties between *trans*- and *cis*-OMCA preclude reversal once a photostationary state is reached. Since OMCA and several other organic additives contain carboxylate functionalities that are directly involved with the viscosity transition, we envisioned using the NAP group to protect this site and thus enable a transition from low to high viscosity upon photorelease that can precede the UV light induced viscosity decrease. We report herein the development of such a system which allows for modulation of solution viscosity in two photochemically orthogonal steps.



Scheme 1 Direct (A) *versus* mediated (B) photoinduced electron transfer photorelease.

In designing this system, we chose to protect the parent *trans*-cinnamic acid compound (tCA) rather than OMCA due to the ease of synthesis of the corresponding NAP–ester (NAP–tCA). NAP–tCA was prepared as the bromide salt due to solubility difficulties with other counterions. We sought to use a visible light absorbing sensitizer for the photorelease step to avoid absorption by or energy transfer to the cinnamic acid moiety. Tris(bipyridyl)ruthenium(II) (Rubpy) was chosen for this purpose due to its strong visible absorption band and aqueous compatibility. To complete the mediated electron transfer scheme, a good electron donor must be included in the system to photogenerate Rubpy^{+1}, a suitable reductant for NAP–tCA (Scheme 2). In the current system, ascorbic acid (ASC) serves as this source. Photorelease of tCA in aqueous CTAB solutions using visible light was expected to induce wormlike micelle formation and thereby a high solution viscosity. Subsequent UV-induced photoisomerization of tCA would reduce the micellar length and thereby cause a drop in viscosity (Scheme 3).

$$\text{Rubpy}^{2+} + \text{ASC} \xrightarrow{h\nu} \text{Rubpy}^{+} + \text{ASC}^{\bullet+}$$

$$\text{Rubpy}^{+} + \text{NAP-tCA} \longrightarrow \text{Rubpy}^{2+} + \text{NAP}^{\bullet} + \text{tCA}^{-}$$

Scheme 2 Deprotection of NAP–tCA by mediated electron transfer.

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† Electronic supplementary information (ESI) available: Synthetic and photolysis procedures, control rheology and photolysis, molecular modeling, mechanistic studies by laser flash photolysis. See DOI: 10.1039/c0cc02203a

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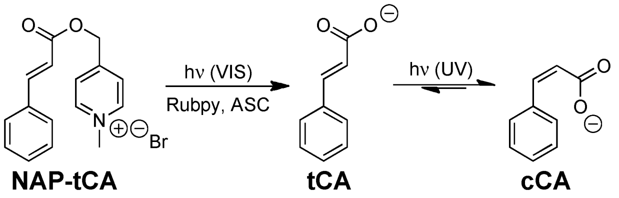

Scheme 3 Photorelease and isomerization of *trans*-cinnamic acid.

Solutions were prepared such that photolysis would generate sufficient tCA to maximize solution viscosity. Samples typically contained 2 mM Rubpy, 30 mM ASC, 30 mM NAP–tCA and 20 mM tCA along with 50 mM of CTAB. Among these components, NAP–tCA and Rubpy had negligible effect on the viscosity; however, ASC reduced the viscosity at high concentrations and therefore its concentration was kept low. The initial solution (Fig. 1A) was a freely-flowing, water-like liquid. Upon irradiation with broad-band visible light (360–800 nm) for 15–60 min, the sample became noticeably viscous (Fig. 1B). Analysis of the irradiated sample by steady-shear rheology (Fig. 2) reveals a substantial (*ca.* 10^5) increase in viscosity at low shear rates. The sample also displays the strong shear-thinning behavior expected of viscoelastic wormlike micellar fluids[18] in contrast to the Newtonian response of the initial solution. Subsequent irradiation with broad-band UV/VIS light (250–800 nm) for 2 h results in an appreciable drop in viscosity, which is evident visually (Fig. 1C) and confirmed by the rheological data (Fig. 2). Note that the drop in viscosity is by *ca.* $10^{2.5}$ at low shear rates and some shear thinning still occurs. This indicates that some moderate-sized micelles are still present.

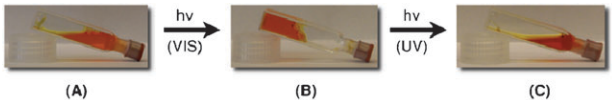

Fig. 1 Photographs of aqueous solutions of CTAB (50 mM), tCA (30 mM), Rubpy (2 mM), and ASC (30 mM) before photolysis (A), after 1 h visible light photolysis (B), and after 2 h UV light photolysis (C).

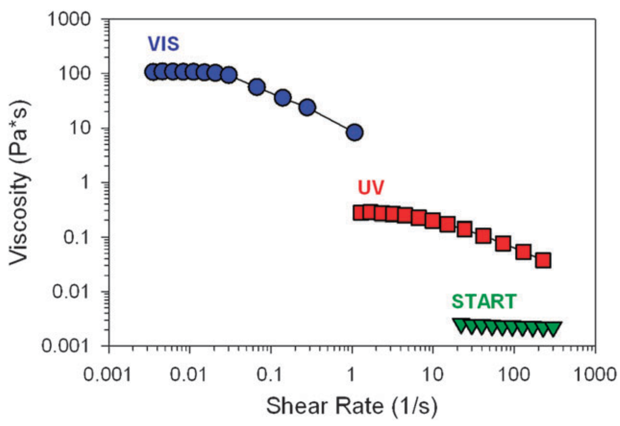

Fig. 2 Steady-shear rheology of the starting solution, after visible irradiation (VIS), and after UV irradiation (UV).[13]

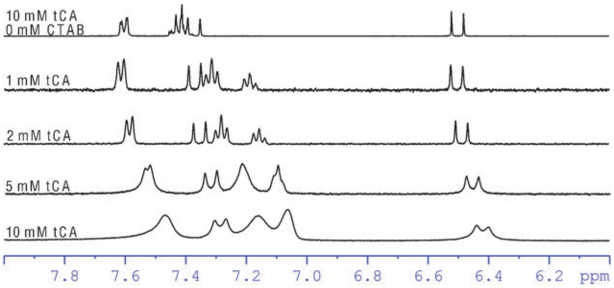

Fig. 3 ^{1}H NMR spectra of 10 mM CTAB solutions in D_2O with added tCA (concentrations as indicated) demonstrating binding of tCA to the micelles. The top-most spectrum contains only tCA for comparison.

That tCA production is responsible for the viscosity increase is supported by several observations. (1) HPLC and NMR analysis confirm release of tCA upon visible light photolysis (Table S1, ESI†). (2) Addition of tCA to CTAB solutions causes viscosity increases similar to those generated from visible light photolysis of the NAP–ester (see ESI†). (3) Finally, addition of tCA to solutions of CTAB in D_2O causes a dramatic broadening and upfield shift in the tCA aromatic and vinylic signals in the ^{1}H NMR spectra (Fig. 3). The NMR data are consistent with the binding of tCA to CTAB micelles, in accordance with similar studies[22] with other aromatic additives. Specifically, an upfield shift of the aromatic protons is observed at 1 mM tCA. Additional shifts and broadening of these peaks at higher concentrations reflect both binding as well as a conversion of spherical CTAB micelles into long entangled wormlike micelles (Fig. 4). A more detailed analysis of these effects will be reported subsequently. As the carboxylate of tCA binds to the cationic headgroup of CTAB, the effective charge is reduced (smaller orange circles) thereby allowing tighter packing of the headgroups and a cylindrical (wormlike) micelle geometry.

Photoreversal of the viscosity increase with UV light is correlated to the conversion of tCA to its *cis* isomer (cCA), as confirmed by HPLC and NMR. cCA has a weaker affinity for CTAB micelles than tCA, leading to its unbinding from the micelles. This is shown by ^{1}H NMR (Fig. 5): the broad and upfield-shifted aromatic ^{1}H NMR signals for tCA gradually return to their unbound downfield values with increasing UV irradiation time. Simultaneously, signals for cCA grow in as the tCA signals diminish. The signals also become sharper as the additives are now in free solution. Unbinding of cCA can be rationalized by comparing the preferred conformations of tCA and cCA. For cCA, the carboxylate group is not coplanar with the aromatic ring, an assertion that is supported by density functional theory calculations (B3LYP/6-31+G(d,p), Fig. S7, ESI†). In contrast, the carboxylate and aromatic moieties of tCA prefer to adopt a coplanar geometry, an important characteristic for binding of aromatic carboxylates to cationic micelles.[17] The unbinding of cCA restores much of the positive charge to CTAB headgroups and the increase in effective headgroup size leads to shorter cylinders or spheres (Fig. 4). Thus, the rheological changes can be understood as originating from these molecular-scale differences. Note that, due to the significant overlap of the absorption spectra for each isomer, complete conversion from *trans* to *cis* is not possible with our apparatus once a photostationary state is

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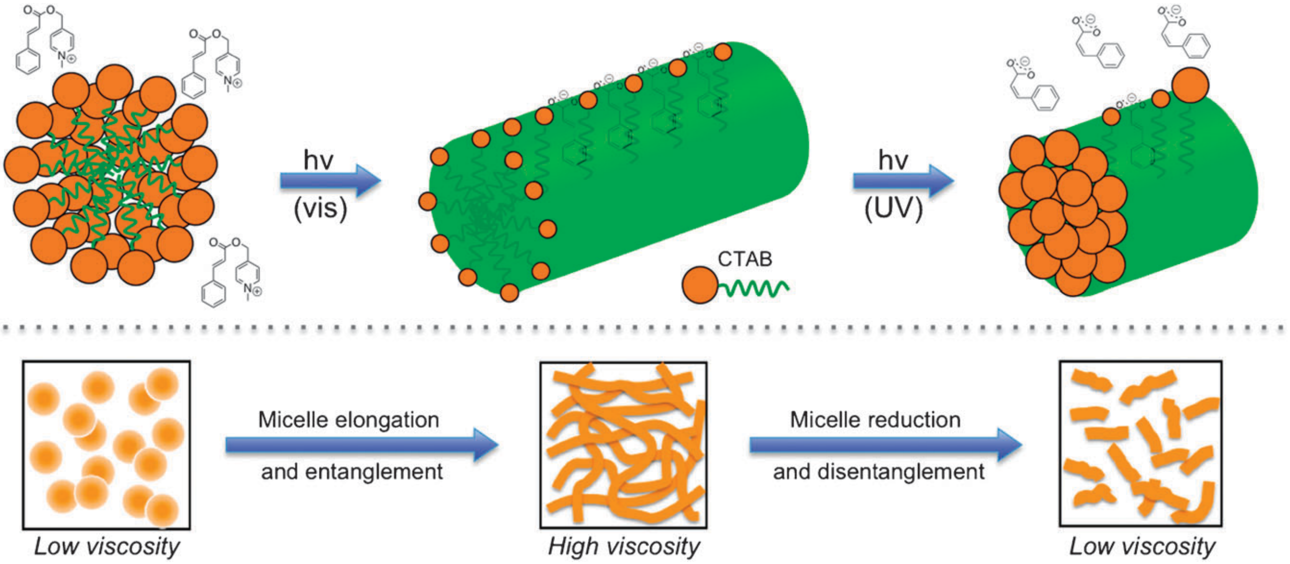

Fig. 4 Changes in micelle structure and corresponding higher-order behavior induced by binding and unbinding of tCA to CTAB.

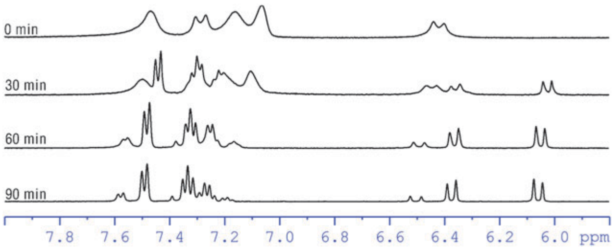

Fig. 5 ^{1}H NMR spectra of 10 mM CTAB and 10 mM tCA in D_2O photolysed with UV light (irradiation periods as indicated) demonstrating production of cCA at the expense of tCA over time and a return of the additives to free solution.

reached. This, in part, is why viscosity is not restored to its starting value following UV irradiation.

In summary, we have applied the NAP photorelease system to control aqueous solution viscosity with two photochemical steps. Large changes in viscosity (10^5 fold increase, $10^{2.5}$ fold decrease) have been observed, and each solution state remains stable for several days. By using visible light to initiate photorelease and UV light to control photoisomerzation, the two viscosity transitions are conveniently orthogonal to one another. Additionally, NMR data have been obtained on a cinnamate-based PR fluid for the first time which validates the viscosity transition mechanism proposed in other cinnamate-based PR fluids. This system may prove useful in specific PR fluid applications and demonstrates the broader utility of the NAP photorelease system for biological or materials applications.

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Application of PET Deprotection for Orthogonal Photocontrol of Aqueous Solution Viscosity

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SUPPORTING INFORMATION

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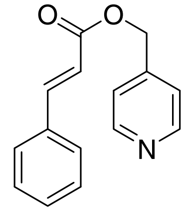
GENERAL EXPERIMENTAL PROCEDURES

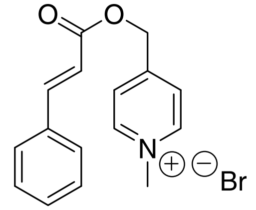
All ^1H and ^{13}C NMR were obtained on a Bruker 400 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to TMS or as indicated. Coupling constants (*J*) are reported in Hertz (Hz). Thin-layer chromatography (TLC) was performed on Merck silica-coated glass plates with UV254 indicator. Compounds were visualized under 254 nm UV irradiation or by treatment with I_2. All flash chromatography was carried out using Silicycle Silia-P Flash Silica Gel (60 Å pore diameter, 40-63 µm particle size). UV-VIS spectra were obtained on a Perkin-Elmer Lambda 2S spectrophotometer. IR spectra were recorded on a Thermo Nicolet IR200 spectrometer. HPLC chromatograms were obtained on a dual Rainin HPXL pump system equipped with a C_{18} reversed-phase column and UV-VIS detector. Elution programs and solvent systems are described in the each respective section.

SYNTHETIC PROCEDURES



Picolyl *trans*-cinnamate

Picolyl *trans*-cinnamate was prepared according to previously reported procedures.[1] **^{1}H NMR** (CDCl$_3$) δ 5.27 (s, 2H), 6.53 (d, *J* = 16.0 Hz, 1H), 7.31 (d, *J* = 5.8 Hz, 2H), 7.40 (m, 3H), 7.55 (m, 2H), 7.78 (d, *J* = 16.0 Hz, 1H), 8.63 (d, *J* = 6.1 Hz, 2H); **^{13}C NMR** (CD$_3$CN) δ 65.1, 118.5, 122.8, 129.3, 130.0, 131.6, 135.3, 146.3, 146.7, 150.9, 167.2 ^{1}H and ^{13}C spectra are in agreement with previously reported spectra.



N-methylpicolinium *trans*-cinnamate bromide (NAP-tCA)

A solution of picolyl *trans*-cinnamate (1.0 g, 4.18 mmol) in anhydrous, distilled acetonitrile (10 mL) was prepared in an oven-dried round bottom flask. The round-bottom flask was equipped with a dry ice condenser filled with isopropanol and dry ice. 2 M bromomethane in *tert*-butylmethyl ether (Aldrich, 6.3 mL, 12.54 mmol) is added to the flask by syringe and the solution is heated to reflux and stirred for 3 h. TLC (1/1 EtOAc/hexanes) after 3 h shows no visible sign of starting material. Ethyl acetate is added to precipitate the crude product. Subsequent recrystallization from ether/chloroform/ethanol (7/2/1) affords white needle-like crystals (1.19 g, 85 %). **Mp** 138-140 °C; **^{1}H NMR** (CD$_3$CN) δ 4.31 (s, 3H), 5.50 (s, 2H), 6.68 (d, *J* = 16.0 Hz, 1H), 7.46 (m, 3H), 7.69 (m, 2H), 7.84 (d, *J* = 16.1 Hz, 1H), 8.00 (d, *J* = 6.4 Hz, 2H), 8.68 (d, *J* = 6.7 Hz, 2H); **^{13}C NMR** (CD$_3$CN) δ 48.9, 64.3, 117.9, 126.1, 129.5, 130.1, 131.9, 135.2, 146.4, 147.1, 157.6, 166.9 ^{1}H and ^{13}C NMR data are in agreement with previously published spectra for the perchlorate and iodide salts.[1]

VISCOSITY CHANGE PHOTOLYSIS PROCEDURES

Materials. NAP-tCA was prepared as described in the Synthesis section. Tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate (Rubpy) was used as received from Strem Chemicals. Ascorbic acid (ASC), cetyltrimethylammonium bromide (CTAB), *trans*-cinnamic acid (tCA) were used as received from commercial sources.

Methods. Photolysis solutions were prepared containing 50 mM CTAB, 0-20 mM tCA/NaOH, 30-50 mM ASC, and 2-5 mM Rubpy in deionized water. tCA was prepared in these solutions through dilution of a stock solution of equimolar tCA and sodium hydroxide in deionized water. 500 µL of the photolysis stock was set aside in the dark as a control. The remaining amount was added to a 1 cm quartz cuvette fitted with a rubber septum. The solution was irradiated with constant stirring for prescribed periods of time by a 300 W tungsten/halogen lamp the output of which is passed through a 360 nm cutoff filter and a Kopp 7093 IR-absorbing filter to ensure visible light irradiation only. UV photolysis of solutions was performed with constant stirring using the unfiltered output of a 350 W Xe arc lamp. Aliquots of the dark control, visible light irradiated, and UV light irradiated samples were removed at the appropriate time for HPLC analysis. Prior to injection, samples were diluted with MeOH/MeCN (1/1) to disrupt any self-assembly in the solutions. HPLC gradient elution using an acetonitrile/acetate buffer (100 mM, pH 4.0) mixture that adjusts from 25% acetonitrile to 70 % acetonitrile over 20 min at a flow rate of 0.5 mL/min was sufficient to resolve the starting material and *cis* and *trans* isomers of the free acid, monitored at 254 nm. Estimated error in integration, 5%.

NOTE: Control experiments revealed a competitive photochemical reaction between Rubpy, ASC, and tCA (see following section "Mechanistic Studies by Laser Flash Photolysis"). Thus, despite quantitative deprotection of NAP-tCA, post-photolysis concentrations of tCA will be less than the sum of the starting concentrations of tCA and NAP-tCA.

Selected Data from Visible and UV Photolysis Experiments

Entry	$[\text{NAP-tCA}]_0$ (mM)[a]	$[\text{tCA}]_0$ (mM)[a]	$[\text{Rubpy}]_0$ (mM)	Photolysis Conditions	VIS NAP-tCA Consumption (%)[a]	VIS [tCA] (mM)[a]	UV [tCA] (mM)[a]
1	51.3	-	5	3 h VIS, 2 h UV	97.0	12.1	4.3
2*	30.7	14.2	5	2 h VIS, 2 h UV	96.7	22.0	7.9
3	31.7	14.0	2	2 h VIS, 2 h UV	97.3	18.8	5.7
4*	28.3	20.5	2	1 h VIS, 2 h UV	95.8	29.9	9.6
5	29.5	18.6	2	10 min VIS	67.8	28.0	-

*Data represent the average of two identical experiments [a]Determined by HPLC, estimated error 5%

Steady-shear Rheology of Photolysis Mixtures:

Rheological studies were performed on a TA Instruments AR2000 stress controlled rheometer using a 20 mm couette geometry, maintained at 20° C by a Peltier-based temperature controller.

NMR ANALYSES OF CTAB/tCA MIXTURES

Addition of tCA to CTAB

50 mM solutions of CTAB were prepared in D_2O with varying concentrations of equimolar tCA and sodium deuteroxide (NaOD). Resonances were referenced to the H_2O residual peak at 4.79 ppm.

UV Light Photolysis

Solutions of 10 mM tCA, 10 mM sodium deuteroxide, and 10 mM CTAB prepared in D_2O were photolysed by broad band UV and visible light (250-800 nm). Spectra were recorded after specific irradiation periods; resonances referenced to H_2O residual peak at 4.79 ppm.

CONTROL EXPERIMENTS

VISIBLE LIGHT PHOTOLYSIS

Control photolyses were performed in the absence of CTAB. Photolysis of aqueous solutions of equimolar Rubpy and NAP-tCA with broad band visible light (360 – 800 nm) resulted in 10 % consumption of NAP-tCA and a negligible amount of free tCA (as determined by HPLC). No detectable amount of photodimerization products was observed by HPLC or NMR in any samples.

UV LIGHT PHOTOLYSIS

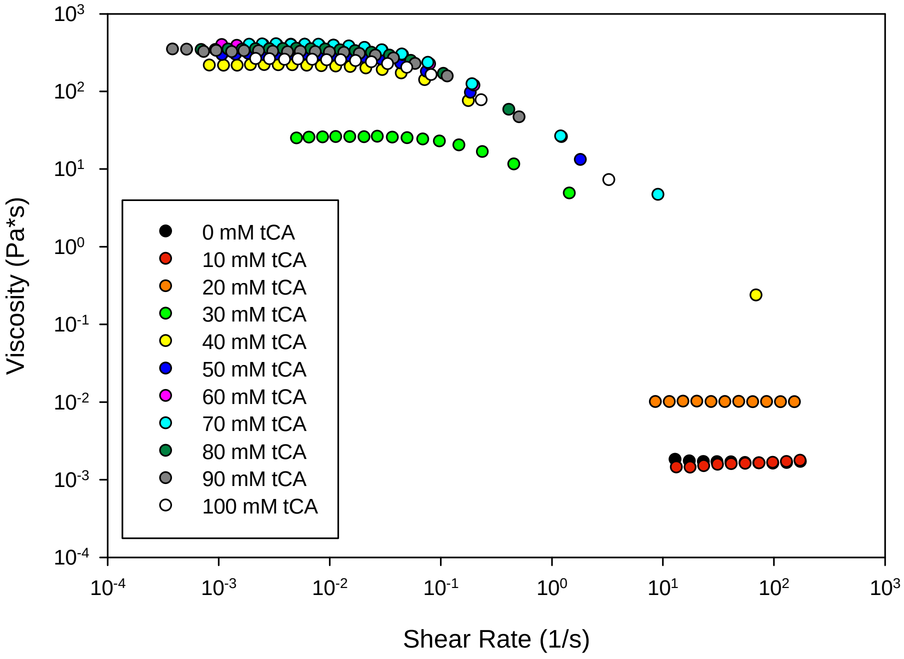
Control solutions of tCA irradiated with unfiltered broad band UV light for 2 h on a Xe arc lamp were converted to the *cis* isomer reaching a final *trans/cis* ratio of approximated 1/2. Solutions of NAP-tCA irradiated with UV light produced a mixture of products including the *cis* isomer of NAP-tCA and a negligible amount of free tCA. No detectable amount of photodimerization product was observed by HPLC or NMR in any samples.

CONTROL RHEOLOGY

CTAB/tCA Standards

Solutions prepared with 50 mM CTAB and varying concentrations of equimolar tCA/NaOH (as indicated) in H_2O.

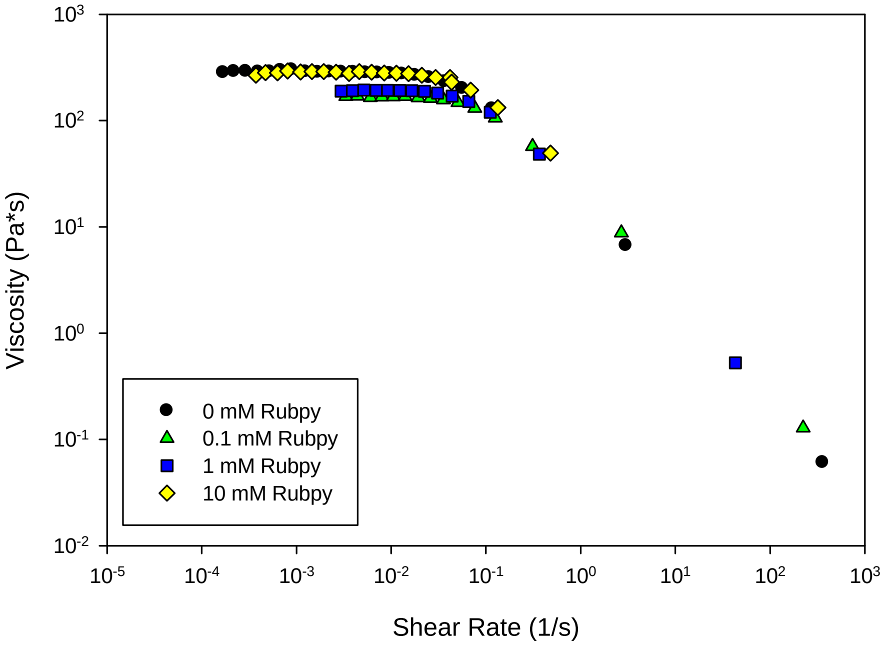
Figure S1.



Effect of Rubpy on Viscosity

Solutions prepared with 50 mM CTAB, 50 mM tCA/NaOH in and varying concentrations of Rubpy (as indicated) in H_2O.

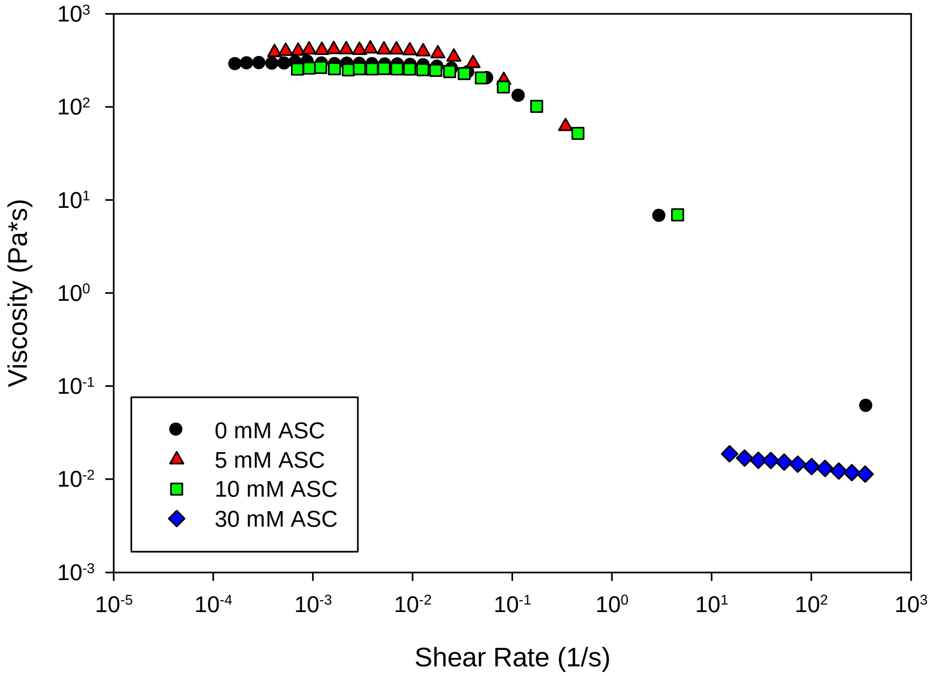
Figure S2.



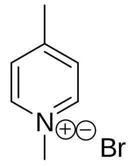
Effect of Ascorbic Acid (ASC) on Viscosity

Solutions prepared with 50 mM CTAB, 50 mM tCA/NaOH, and varying concentrations of ASC (as indicated) in H_2O.

Figure S3.



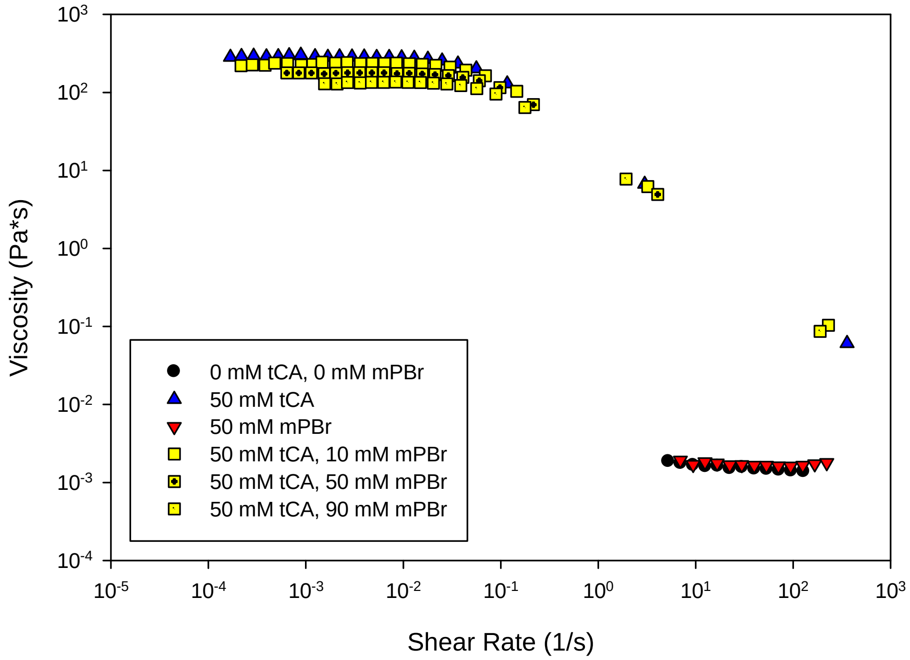
Effect of NAP-photorelease Byproduct on Viscosity



mPBr

Solutions prepared with 50 mM CTAB and varying concentrations of equimolar tCA/NaOH and 4-methylpicolinium bromide (mPBr) (as indicated) in H_2O.

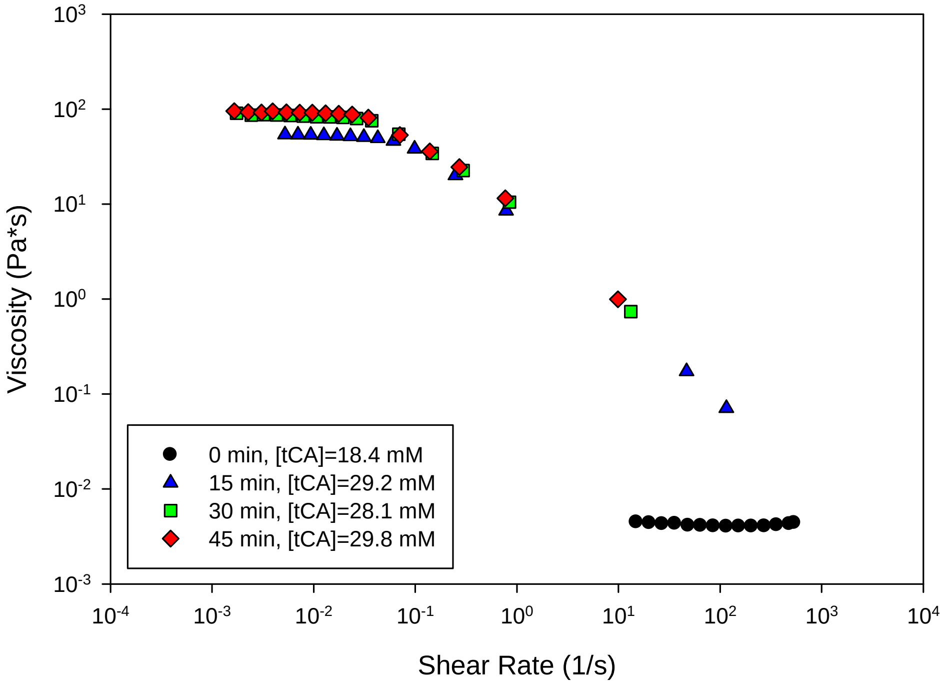
Figure S4.



Effect of VIS Irradiation Time on Viscosity

Solutions were prepared with 50 mM CTAB, 30 mM NAP-tCA, 20 mM tCA/NaOH, and 30 mM ASC in H_2O and photolyzed with broad band visible light (360-800 nm) with stirring for varying periods of time (as indicated). Concentrations listed for each time period are post-photolysis concentrations of tCA as determined by HPLC (see photolysis procedures).

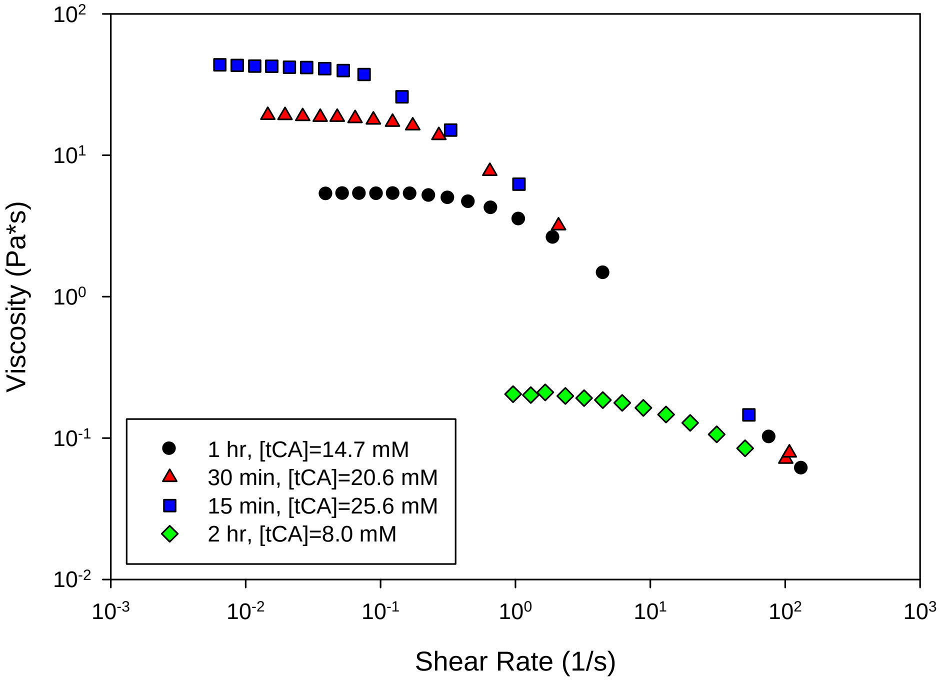
Figure S5.



Effect of UV Irradiation Time on Viscosity

Solutions were prepared with 50 mM CTAB, 30 mM NAP-tCA, 20 mM tCA/NaOH, and 30 mM ASC in H_2O and photolyzed with broad band visible light (360-800 nm) with stirring for 1 h. Each solution was subsequently irradiated with broad band UV light (250-800 nm) for various periods of time (as indicated). Concentrations listed for each time period are post-photolysis concentrations of tCA as determined by HPLC (see photolysis procedures).

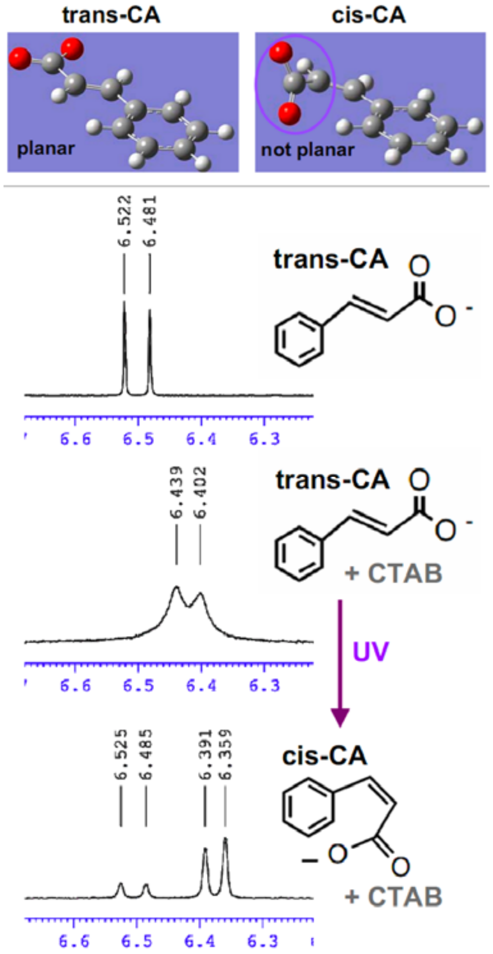
Figure S6.



MOLECULAR MODELING

Figure S7 shows minimum energy geometries, optimized at the B3LYP/6-31+G(d,p) level of density functional theory[2] for the *cis* and *trans* isomers of the cinnamate ion. That these stationary points correspond to local minima was confirmed by a vibrational energy calculation which showed no imaginary frequencies in either case. The *trans* form is predicted have a planar structure where the phenyl ring, the C=C double bond, and the carboxylate group all maintain a stabilizing conjugative interactions. On the other hand, the *cis* form is predicted to be non-planar as the carboxylate group rotates out of plane to avoid a steric clash with the phenyl C-H bonds that are *ortho* to the alkenyl group.

Figure S7.



MECHANISTIC STUDIES BY LASER FLASH PHOTOLYSIS (LFP)

Methods. Samples were prepared in deionized water containing 10% MeOH and sufficient Rubpy was added such that the optical density at the excitation wavelength, 532 nm, was 0.5-0.6. The prepared samples were placed in a 1 cm quartz cuvette and sealed with a rubber septum. Samples were stirred continuously during photolysis. An Nd:YAG laser capable of 532, 355, and 266 nm pulses between 4-6 ns duration was used as the excitation source. A 350 W Xe arc lamp was used as the probe beam passed through a monochromator to a PMT detector. A 350 MHz digital oscilloscope was used to observe the traces which were subsequently recorded on a personal computer. Growth and decay curves were fit to model functions using the MathCAD software package.

Discussion. Experiments to ascertain the success of the desired electron transfer reactions and gather information about the side reaction were performed. Previous studies have shown the effective quenching of Rubpy* by ASC to generate Rubpy^{+1}.[3,4] Confirming control deprotection photolysis experiments that combined Rubpy with tCA, Rubpy luminescence was not quenched with added tCA. Thus, both the productive release of tCA from NAP-tCA and the side reaction appear to occur from Rubpy^{+1} and we turned to LFP quenching studies.

LFP solutions were prepared with a fixed amount of Rupby (0.8 mM) and a large excess of ASC (1 M) to ensure adequate production of Rubpy^{+1}. Each solution contained 50 mM CTAB to ensure full solubility of ASC and tCA, however 10 % methanol was added to avoid the formation of micelles. Increasing amounts of Rubpy^{+1} quencher (NAP-tCA or tCA) were added to these solutions and the growth and decay of Rubpy^{+1} was monitored at 510 nm. Traces were fit to a model function containing exponential growth and decay terms with an added baseline correction term. (Equation 1)

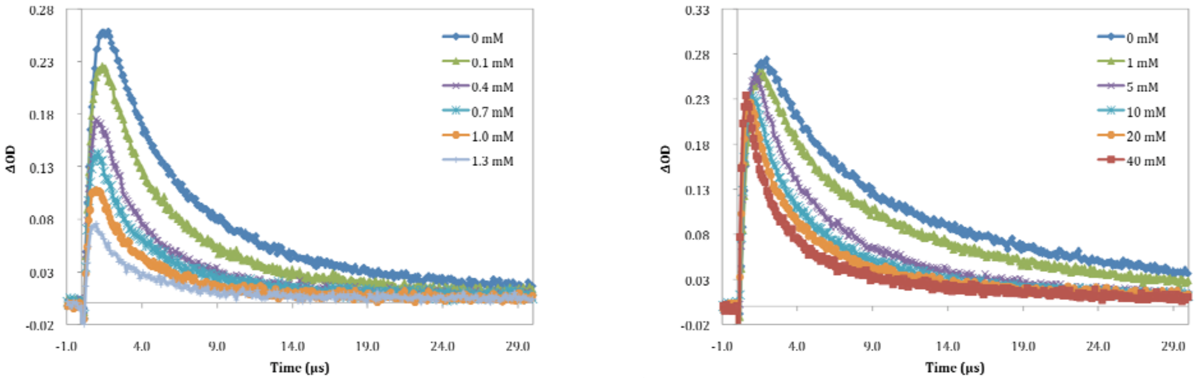


Figure S8: Transient absorption traces from 532 nm pulsed laser photolysis, monitored at 510 nm with varying concentrations of (LEFT) NAP-tCA or (RIGHT) tCA

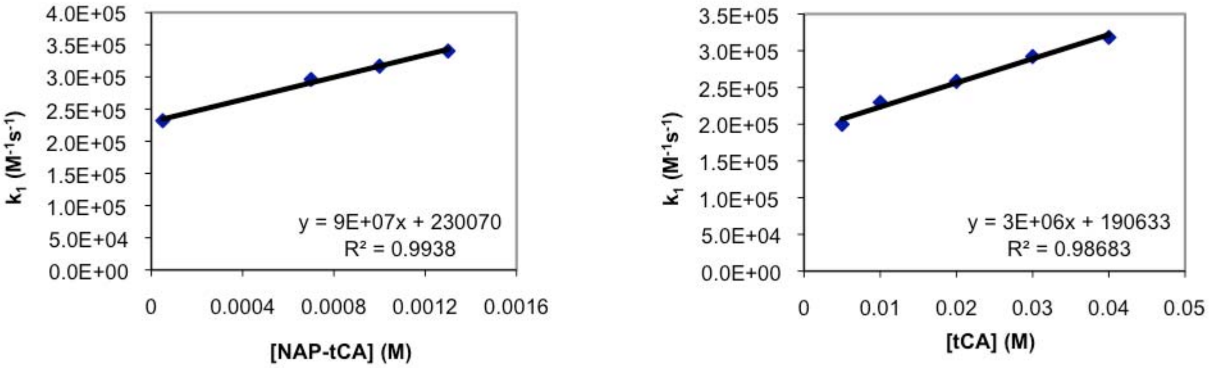


Figure S9: k_1 versus (LEFT) [NAP-tCA] or (RIGHT) [tCA] from quenching of LFP signals at 510 nm

$$O.D. = A + OD_0\left(\frac{k_1}{k_2 - k_1}\right)\left(e^{-k_1 t} - e^{-k_2 t}\right) \qquad (1)$$

Both tCA and NAP-tCA quench the signal from Rubpy^{+1} (Figure S8), indicating that electron transfer from Rubpy^{+1} to either compound are possible mechanistic pathways. The rates of decay for each of the curves were plotted versus quencher concentration to determine the quenching rate constant of each process. (Figure S9) The electron transfer process from Rubpy^{+1} to NAP-tCA (k_q= 9 x 10^7 $M^{-1}s^{-1}$) is apparently an order of magnitude greater than electron transfer to tCA (k_q = 3 x 10^6 $M^{-1}s^{-1}$). Thus, electron transfer to NAP-tCA is the dominant process, however, an order of magnitude smaller difference in k_q for quenching of Rubpy^{+1} by tCA indicates that this process is still fairly competitive when present in significant concentrations. It is likely that electron transfer to tCA is the dominant process leading to diminishment in tCA concentration during prolonged irradiation periods. However, the identity of the final products as a result of this process is unclear.

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