Substituting Coumarins for Quinolinones: Altering the Cycloreversion Potential Energy Landscape

Nicholas Paul, † Man Jiang, ‡,§ Nikolai Bieniek, † J. Luis Pérez Lustres, † Yang Li, † Nikolaus Wollscheid, † Tiago Buckup, † Andreas Dreuw, ‡,§ Norbert Hampp,*,‡,§ and Marcus Motzkus †,‡

‡Physikalisch-Chemisches Institut, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany
§Interdisziplinäres Zentrum für Wissenschaftliches Rechnen und Physikalisch-Chemisches Institut, Ruprecht-Karls Universität, Im Neuenheimer Feld 205, 69120 Heidelberg, Germany
†Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany

Supporting Information

ABSTRACT: The light-activated cleavage of cyclobutane-based systems via [2 + 2] cycloreversions, such as thymine and coumarin dimers, is an important but still poorly understood ultrafast photochemical reaction. Systems displaying reversible cycloreversion have found various uses in cross-linked polymers, enhancing gas adsorption affinities in inorganics, and light-activated medical therapies. We report the identification of a heterogeneous mode of cycloreversion for a rarely examined coumarin analogue system. Quinolinone monomers and dimers were probed using ultraviolet pumped, transient absorption spectroscopy and demonstrated radically different photophysical properties than coumarins. Monomers displayed enhanced intersystem crossing at almost 1:1 versus the combined nonradiative and radiative singlet decay, while the dimers underwent cycloreversion to a one excited—one ground state monomer photoproduct pair. The change in both systems was directly linked to the lactame group in the quinolinone motif. This discovery highlights the dramatic effects that small chemical changes can have on photoreaction pathways and opens up a new means to produce and develop more efficient cycloaddition–cycloreversion systems.
and characterized the quinolinone monomer (Figure 1B). One excited singlet state monomer product pair. Formation from a homogeneous pair of monomers in a formed. Lactone to lactame substitution switched the product the nature of the ring-cleaved, monomer photoproducts and discussed give strong evidence as to the ability of changing dimer ring cleavage mechanism. The results to be presented coumarin monomers), but it also substantially altered the fl substitution not only contributed primarily to increased related coumarins. The lactone to lactame functional group both the quinolinone monomer and dimer compared to the Analysis of the resulting data showed substantial di sulfoxide-dihydroxyquinolin-2(1H)-one. Additionally, we also studied the structure has been numbered to show the standard IUPAC 3-sulfoxide-

Figure 1. (A) Molecular structure of the syn-h.t quinolinone monomer stereoisomer. (B) Molecular structure of the corresponding quinolinone monomer (7-methoxy-1-methylquinolin-2(1H)-one). The structure has been numbered to show the standard IUPAC numbering for this molecular motif.

expect to induce a noticeable change in the ring cleavage process when substituting the more electronegative oxygen in coumarin for a nitrogen in the quinolinone. The results of the study used the same UV pump−visible probe transient absorption technique as used for the previous study of coumarin dimer stereoisomers. Additionally, we also studied and characterized the quinolinone monomer (Figure 1B). Analysis of the resulting data showed substantial differences in both the quinolinone monomer and dimer compared to the related coumarins. The lactone to lactame functional group substitution not only contributed primarily to increased fluorescence of the quinolinone monomer (compared to coumarin monomers), but it also substantially altered the dimer ring cleavage mechanism. The results to be presented and discussed give strong evidence as to the ability of changing the nature of the ring-cleaved, monomer photoproducts formed. Lactone to lactame substitution switched the product formation from a homogeneous pair of monomers in a thermally hot ground state to a heterogeneous, one ground−one excited singlet state monomer product pair.

## EXPERIMENTAL SECTION

### Materials for Molecular and Ring Cleavage Quantum Yield Studies.
Methyl iodide (99%, Alfa Aesar), sodium hydride (60% suspension in paraffin wax, Sigma-Aldrich), meta-anisidine (98%, Alfa Aesar), cinnamoyl chloride (98%, Acros Organics), aluminum chloride (purum, Merck), dimethylformamide (purum, Acros Organics), dichloromethane (99.8%, Acros Organics), magnesium sulfate (p.a., Sigma-Aldrich), and sodium chloride (tbc. Sigma-Aldrich) were used as received. Dichloromethane and acetonitrile (99.9% Acros Organics) were used for photochemical reactions. Acetonitrile for analytic HPLC measurements was gradient grade (VWR Chemicals); for all other experiments solvents were of technical quality and purified by distillation prior to use.

### Preparation of 7-Hydroxyquinolin-2(1H)-one. 7-Hydroxyquinolin-2(1H)-one was prepared following a literature procedure.30 Yield: 64%. 1H NMR (300 MHz, dimethyl sulfoxide-d6): δ/ppm = 6.21 (d, J = 9.1 Hz, 1H, CH), 6.62 (d, J = 8.5 Hz, 1H, CH), 6.69 (d, J = 2.2 Hz, 1H, CH), 7.44 (d, J = 8.5 Hz, 1H, CH), 7.73 (d, J = 9.4 Hz, 1H, CH), 10.08 (s, 1H, OH), 11.48 (s, 1H, NH).

### Preparation of 7-Methoxy-1-methylquinolin-2(1H)-one. 7-Methoxyquinolin-2(1H)-one (9.29 g, 0.06 mol) was suspended in 80 mL of dimethylformamide under inert conditions. The suspension was cooled to 0 °C, and sodium hydride (60% suspension in paraffin wax, 4.88 g, 0.12 mol, 2.2 equiv) was slowly added. The suspension was stirred for 15 min followed by dropwise addition of methyl iodide (7.5 mL, 0.12 mol, 2.1 equiv). The reaction vessel was stirred for 1 h and the solvent removed under reduced pressure. The remaining solid sample was dissolved in ethyl acetate followed by extraction with water and brine. The organic layer was dried over magnesium sulfate and the solvent removed under reduced pressure. The solid sample was recrystallized from dichloromethane giving 4.96 g (5.6 mmol, 25%) of the solid syn-head-to-tail 7-methoxy-1-methylquinolin-2(1H)-one product.

### Preparation of syn-Head-to-Tail 7-Methoxy-1-methylquinolin-2(1H)-one Dimer. 7-Methoxy-1-methylquinolin-2(1H)-one (8.5 g, 0.05 mol) was dissolved in 100 mL of dried and degassed acetonitrile. The reaction vessel was irradiated in the photoreactor for 48 h. The formed precipitate was filtered off and washed with methanol leaving 2.12 g (5.6 mmol, 25%) of the solid syn-head-to-tail 7-methoxy-1-methylquinolin-2(1H)-one dimer product.

### Dimerization Reactions. The dimerization reactions were performed in an air-cooled Rayonet-type photoreactor equipped with 16 Osram Eversun 40 W/79K UV fluorescent tubes (λmax = 350 nm). The reaction process was monitored via HPLC performed on an Ultimate 3000 system (Dionex) equipped with a diode array detector. An RP-18 column was used with a 75:25 (v/v) mixture of acetonitrile and water as an eluent.

### NMR Spectroscopy. 1H NMR spectra were measured on an AV-300 (300 MHz, Bruker), respectively, and AV-500 (500 MHz, Bruker) for the dimers. Dimethyl sulfoxide-d6 was used as solvent. The δ chemical shift was calibrated using the residual solvent peak.

### Steady-State Spectroscopic Characterization and Fluorescence Quantum Yield Estimation. UV/vis spectra of the samples were recorded on a Cary 100 (Agilent Technologies) spectrophotometer. Photoluminescence spectra were recorded with a Varian Cary Eclipse (Agilent Technologies). The fluorescent standard used was Coumarin 120 in the same solvent, acetonitrile. Anhydrous grade acetonitrile was used and extracted from the solvent container under a strong nitrogen purge. Samples were measured using an ultramicro quartz cuvette with 2 mm path length (105.250-15-40, Hellma-Analytics) for both absorption and fluorescence measurements.

### Determination of the Quantum Yield of the syn-Head-to-Tail 7-Methoxy-1-methylquinolin-2(1H)-one Dimer. The cycloreversion reaction of the quinolinone dimer to monomer photoproducts was monitored and analyzed using UV/vis-spectroscopy. UV/vis spectra of the samples were recorded on a Lambda 35 spectrophotometer (PerkinElmer). The quinolinone solution in acetonitrile was irradiated using a UV-LED (λ = 265 nm; Thorlabs). The light intensity was determined using a photodiode (S1337-1010BQ, Hamamatsu). The irradiated sample area was kept constant using a cover, and the sample was stirred throughout the experiments.
Femtosecond Transient Absorption Experiments. The setup used was based on a tunable UV pump source and a broadband supercontinuum for the wavelength selective probing. As a light source, a regenerative Ti:sapphire amplifier system (CPA 1000, Clark-MXR, Inc.) was used to deliver 800 nm pulses with 640 μJ per pulse and a repetition rate of 1 kHz. To generate UV pump pulses, 300 μJ of the fundamental 800 nm was used to pump a two-stage nonlinear optical parametric amplifier (NOPA) generating visible pulses.31,32 The visible pulses were overcompressed by a pair of fused silica prisms in order to compensate for all dispersive optical elements after the second harmonic crystal for UV generation, which has been described previously.33,34 After compression, the visible pulses were frequency doubled in a BBO crystal with 55 μJ energy at 4 kHz repetition rate. About 0.650 mJ per pulse and a repetition rate of 1 kHz.

Global Analysis of the Transient Absorption Data. Transient absorption data were preprocessed using a combination of a 5 × 5 moving average filter and SVD to minimize noise contributions to the data (see the Supporting Information). Coherent artifact was removed by using an acetonitrile solvent background. Transient absorption data were corrected for the chirp of the white-light continuum with the help of the nonresonant coherent solvent signal.35 The resulting transient data were globally fitted with a multi-exponential function and basis functions describing the coherent contribution at early time. The set of exponential functions and decay-associated difference spectra (DADS) were transformed into time-dependent concentrations and evolution-associated difference spectra (EADS) under the assumption of an underlying kinetic model and by assignment of the fitted decay times to microscopic rate constants of the mechanism. All fitting procedures were self-programmed in Matlab R2016a. See the Supporting Information for further details.

Quantum Chemical Calculations of the Quinolinone Monomer and Dimer Species. To assist in the data analysis, quantum chemical calculations were performed for three model systems. The equilibrium geometries of the quinolinone dimer and monomer (Figure 1A and B) were optimized using density functional theory (DFT) with the B3LYP-D3 exchange-correlation functional and the 6-31G* basis set.36,37 A quinolinone monomer devoid of the α,β-unsaturated carbonyl group, where only a single bond exists between carbon atoms 3 and 4 (see Figure 1B for atomic labeling) and the valence sites on each carbon contain a methyl group, was also computationally studied (see Supporting Information Figure S5). This model compound is representative of the quinolinone dimer cleaved across the cyclobutane ring but maintains the same degree of σ-conjugation and is used as a reference for investigating the presence or absence of excitonic coupling within the quinolinone dimer (dubbed reference monomer for the remainder of this paper). Vertical excitation energies were calculated using time-dependent DFT (TDDFT),38 with and without implementation of the Tamm–Dancoff approximation (TDA),39 and in combination with the B3LYP, BHLYP,40 and CAM-B3LYP exchange-correlation functionals as well as configuration interaction singles with perturbative doubles (CIS(D))40 and the algebraic diagrammatic construction scheme for the polarization propagator at second-order level (ADC(2)).41–43 All calculations employed the 6-31G* basis set and were performed using the Q-Chem 5.0 package.44

RESULTS

The quinolinone dimer in question (Figure 1A) undergoes cycloreversion across the cyclobutane ring to yield two
quinoxaline monomer units (Figure 1B). The dimer and monomer contain the same hydrocarbon σ-bond manifold, with the obvious differences at the carbon positions where the bridging cyclobutane ring exists in the dimer but not in the monomer. However, as can be seen in Figure 1, the σ-system differs, with an extra C=C double bond across the carbon 3 and 4 positions in the case of the monomer. This typical monomer–dimer structural relationship, and nomenclature, is customary in systems that undergo cycloreversion and cycloaddition. The main results will be discussed in the following order: steady-state spectroscopic characterization, density functional theory, and finally time-resolved spectroscopic experiments. Extra figures, including all raw transient absorption data, are given in the Supporting Information.

**Steady-State Absorption Spectra, Photoluminescence, and 2D NMR Characterization.** Absorption spectra for both the dimer and the monomer are given in Figure 2A (see also Figure S1 in the Supporting Information for comparison with the absorption spectra for the coumarin monomer and dimer studied previously49). Dimer stereochemical purity, following molecular synthesis, was checked by NOESY NMR (Figure S2), which showed the dimer to be isolated in the syn-ht stereoisomer. Consequently, the absorption spectrum relating to the quinolinone dimer is indicative of only the syn-ht stereoisomer. The dimer absorption (Figure 2A, black trace) from 240 nm onward shows significant absorption up until about 305 nm with an absorption onset of about 315 nm. By contrast, the quinolinone monomer (Figure 2A, blue trace) shows signiﬁcant absorption extending until 350 nm with an onset at about 360 nm. The red-shifted absorption in the monomer arises from the extended π-conjugation across the carbon 3 and 4 positions. The same extension of the absorption to longer wavelengths has been observed for coumarin monomer systems. As with other known systems,15 single-photon cycloreversion of the dimer can occur when exposed to a short-wavelength photon, which in this system must be ≤315 nm. Likewise, irradiation of the monomer at wavelengths between 320 and 350 nm, resonant with the valence state, will lead to the cycloaddition reaction and accumulation of the dimerized photoproduct.47 The photoluminescence spectrum of the quinolinone monomer is shown in Figure 2A. Attempts to measure the photoluminescence of the syn-ht quinolinone dimer stereoisomer were unsuccessful. Measurements showed only emission characteristic of the quinolinone monomer or nothing at all. We assigned observable, weak emission from the monomer as originating from degraded dimer in the sample and/or product formed from the actual photoluminescence experiment itself. The origin of this does not detract from the observation: emission from the dimer itself was not observed, and hence the dimer can be considered as nonemissive. The photoluminescence activity of unsubstituted coumarin is also known to be extremely low or practically nonemissive.48−50 In contrast, quinolinone monomer displayed a relative fluorescence quantum yield of ≈5% in acetonitrile (see Figures S3–S4 for details), which is in accordance with previous literature.51

**Quantum Chemical Calculations.** Further insight into the fundamental electronic structure of the quinolinone monomer was obtained using quantum chemical calculations. The excitation energies for the lowest energy singlet and triplet states were calculated using a variety of computational methods (see Table S1). Inspection of the excitation energies and the intensities showed that, relative to the benchmark method of ADC(2), the less computationally demanding TDA/TDDFT/CAM-B3LYP agreed favorably and was used for further calculations. Thus, for the rest of this paper, all transitions are represented using Lorentzian curves and a full width at half-maximum of 10 nm.

![Figure 2](image-url)  
**Figure 2.** (A) Raw absorption (Abs) and emission spectra (PL) for the quinolinone dimer and monomers studied. (B) Calculated absorption spectra for the quinolinone monomer (blue trace), dimer (black trace), and reference monomer (ref. Monomer, yellow trace) which is devoid of the αβ double bond between carbons 3 and 4. Alongside is the calculated fluorescence spectrum of the quinolinone monomer (orange trace). Calculated spectra were obtained using TDDFT/CAM-B3LYP/6-31G* and shifted by −0.74 eV to compensate for missing solvation effects. The transitions are represented using Lorentzian curves and a full width at half-maximum of 10 nm.

### Table 1. Calculated Vertical Excitation Energies (in eV) of the Energetically Lowest Singlet States of the Quinolinone Monomer, Dimer, and Reference Monomer*$^a$

<table>
<thead>
<tr>
<th>state</th>
<th>quinolinone monomer</th>
<th>quinolinone dimer</th>
<th>reference monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BHLYP</td>
<td>CAM-B3LYP</td>
<td>BHLYP</td>
</tr>
<tr>
<td>S$_0$</td>
<td>4.64 (0.32)</td>
<td>4.49 (0.28)</td>
<td>5.08 (0.04)</td>
</tr>
<tr>
<td>S$_1$</td>
<td>5.20 (0.05)</td>
<td>4.95 (0.00)</td>
<td>5.28 (0.17)</td>
</tr>
<tr>
<td>S$_2$</td>
<td>6.60 (0.14)</td>
<td>5.85 (0.12)</td>
<td>5.39 (0.04)</td>
</tr>
<tr>
<td>S$_3$</td>
<td>6.47 (0.67)</td>
<td>6.33 (0.67)</td>
<td>5.57 (0.08)</td>
</tr>
<tr>
<td>S$_4$</td>
<td>5.30 (0.00)</td>
<td>5.06 (0.06)</td>
<td>5.30 (0.01)</td>
</tr>
<tr>
<td>S$_5$</td>
<td>5.28 (0.17)</td>
<td>5.07 (0.17)</td>
<td>6.82 (0.23)</td>
</tr>
</tbody>
</table>

*aOscillator strengths and characters for the S$_0$ → S$_n$ transitions are given in parenthesis.
results are based on the TDA/TDDFT methods primarily using the CAM-B3LYP exchange-correlation functions. Electronic excitation energies were, subsequently, calculated for the quinolinone monomer, quinolinone dimer, and reference monomer subunit containing a π-electronic system more similar to one-half of the quinolinone dimer unit (see Figure S5). The excitation energies calculated for the three systems are given in Table 1. These values have been used in Figure 2B to generate theoretical absorption spectra. Continuing with the quinolinone monomer, the lowest excited state \( S_1 \) is of \( ππ^* \) character and is representative of the HOMO–LUMO transition corresponding to the bands at 315–350 nm. Due to the neglect of vibrational and solvation effects, the absolute values in Table 1 cannot be expected to perfectly match the experimental values.\(^{52} \) Additionally, it cannot be ruled out that the methods used can intrinsically generate over/under-estimations of the energy levels based on approximations made within the physical models used. However, despite these issues, application of a constant offset of \(-0.74\) eV to the values gives a very good agreement between the position of the calculated peaks and the average position of the bands in the raw absorption spectra.

A difference in results can be seen between use of the BHLYP and CAM-B3LYP basis functions. First, in all instances the BHLYP method gives more blue-shifted excitation energies than the CAM-B3LYP method. This suggests that the BHLYP method is more prone to overestimation of the excitation energies. Second, the next optically allowed transition is different in both methods. For the CAM-B3LYP method it is the \( S_2 \) state which is allowed, whereas the BHLYP predicts that the \( S_3 \) is optically allowed. Closer inspection of the calculated values in Table S1 shows that in general the CAM-B3LYP methods have a much more consistent offset from the experimental data, and hence it is used to reproduce the theoretical absorption spectra in Figure 2B. Assuming the CAM-B3LYP has more accurately resolved the locations of the valence transitions, from \( S_0 \) to \( S_1 \), the \( S_2 \) state is an optically dark \( ππ^* \) transition, while the \( S_3 \) state is a weakly active \( ππ^* \) state. Furthermore, the emission spectrum was also simulated for the quinolinone monomer (Figure 2B and Table 2) using the same energetic shift and was found to agree very well with the position of the measured emission spectrum.

The lowest energy excited states of the quinolinone dimer, \( S_0 \) and \( S_2 \), are blue-shifted with respect to the monomer, which shows the same trend observed in the raw spectra due to less \( π \)-conjugation. The \( S_1 \) and \( S_2 \) transitions are \( ππ^* \) in nature; however, the states are inherently mixed due to multiple orbital contributions. The reference monomer, which mimics one-half of the quinolinone dimer in terms of absolute \( π \)-conjugation, has calculated excitation energies that are all blue-shifted to higher energies than either the quinolinone dimer or monomer. This is interesting when comparing to the dimer, as it suggests that the quinolinone dimer \( π \)-systems, on each half of the molecule, exhibit through space electronic coupling.

**Table 2. Calculated Vertical Emission Energies (in eV) of the Quinolinone Monomer (Right Column, \( S_i(eq) \)) Compared with the Energies of Absorption (Left Column, \( S_0(eq) \))\(^a\)**

<table>
<thead>
<tr>
<th>state</th>
<th>quinolinone monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_0 )</td>
<td>( 4.49 (0.28) )</td>
</tr>
<tr>
<td>( S_1 )</td>
<td>( 4.95 (0.00) )</td>
</tr>
<tr>
<td>( S_2 )</td>
<td>( 5.08 (0.06) )</td>
</tr>
<tr>
<td>( S_3 )</td>
<td>( 5.85 (0.12) )</td>
</tr>
<tr>
<td>( S_4 )</td>
<td>( 6.33 (0.67) )</td>
</tr>
</tbody>
</table>

\(^a\)\( S_0 \rightarrow S_1 \) oscillator strengths are quoted in parenthesis.
quinolinone dimer excited at 280 nm (Figure 3C) shows an extremely broad ESA that spans the whole probe range and persists until 6−7 ps after which the data show clear signals reminiscent of photocleaved monomer in the excited singlet state.

Examination of the quinolinone monomer spectra (Figure 4A) and dynamics (Figure 4B) better describes the dynamics quantitatively. Starting with the monomer spectra, the early-time subpicosecond ESA identified in Figure 3B is seen as the dark blue spectrum in Figure 4A at 80 fs, which is just after the instrument response of this measurement (ca. 60 fs). Within 0.2 ps this signal decays toward zero in the 370−460 nm spectral region and can be seen by looking at the 435 nm transient (Figure 4B, green). The rapid decay is characteristic of excitation to a higher lying singlet state. This is also apparent in the 384 nm transient (Figure 4B, blue), but in this case the signal inverts to negative amplitude as it is overlapped with the monomer SE band. From 0.1 to 150 ps the spectra display the negative SE peak, which is indicative of population of an emissive singlet state. Furthermore, the spectra undergo a shift to the blue across a period of ca. 20 ps (see Figure 4B). Finally, the data show the growth of a new absorbing species, which results in an observable lifetime of 500 ns. The TA data for the quinolinone monomer excited at 320 nm are almost the same as in the 280 nm case with two exceptions. As is indicated in Figures 3A and 3B, the data for the 320 nm excitation show an absence of the short-time (<0.2 ps) ESA indicating a difference in singlet state population upon excitation. However, Figure 5 shows selected spectra for the monomer excited at 320 nm, which also shows more clearly the absence or reduction in the presence of the blue-shift for the emissive singlet state signature. This absence of the spectral shift allows one to see the presence of an isosbestic point at 362 nm which is present due to the singlet to triplet intersystem crossing taking place.

Quinolinone dimers show a more drastic change in the TA data (see Figure 6). In the first 80 fs a broad ESA feature can be seen spanning the entire probed region. The ESA displays a noticeable minimum, or well, at the same position as the quinolinone monomer SE. By 1 ps, the ESA has decayed, and the TA signal looks highly reminiscent of the quinolinone monomer, exhibiting all the characteristic SE and ESA signatures seen previously. The only noticeable difference lies in the spectral region below 340 nm, where the signal shows a new ESA band which remains largely static with no obvious transient behavior. The data in this region are to be taken with a fair degree of uncertainty, as the supercontinuum probe used is particularly low in intensity, and therefore artifacts due to modulating pump−probe overlap and chromatic divergence in the probe may arise. For the remaining time range measured, the data follow that of the quinolinone monomer, displaying more fine structure in the spectra reminiscent of the monomer excited at 320 nm rather than at 280 nm.
the model development, SVD analysis was performed to give dimer system, a global target analysis was performed. Prior to the dynamics occurring in the quinolinone monomer and to the transition from the S3 state to the S1 state. The 280 nm excitation, the rapid nonradiative relaxation is assigned indicative of the S1 manifold. This is justi
ted not only by its short lifetime but mainly due to its exclusive excitation with shorter wavelengths (280 nm). The assignment is further supported by the theoretical calculations, which predict that the two lowest energy optical transitions would be separated on the order of 0.59 eV (c.a. 4760 cm\(^{-1}\)). This energy separation matched that observed in the raw data, as the cluster of well-defined absorption peaks between 310 and 350 nm and a weaker band centered at 285 nm overlaps with the predicted optical excitation energies. Quantum chemical calculations propose that the origin of the higher energy, short-lived S\(_N\) state is the S\(_T\) state, where the S\(_T\) exhibits no appreciable optical cross section. Therefore, in the case of the 280 nm excitation, the rapid nonradiative relaxation is assigned to the transition from the S\(_T\) state to the S\(_N\) state. The subsequent blue-shift observed in the data from 1 to 20 ps is indicative of vibrational relaxation within the S\(_N\) manifold. The lack of a blue-shift in the 320 nm data (Figure 3A and S) reinforces this, as one would expect there to be population of multiple excited state vibrational levels upon population of the S\(_N\) state from the S\(_T\) relaxation process. Finally, the S\(_T\) state exhibits a significant degree of intersystem crossing to the T1 triplet manifold.

For the quinolinone dimer, the TA data is dominated in the short time (<1 ps) by an ESA originating from the dimer S1 state (Figure 3C and S). Following the decay of the dimer ESA, the resulting monomer TA spectra indicate that the dimer cleavage has formed monomer in the excited S1 state. The cleavage from a 280 nm excitation can at most produce the time-dependent concentrations, and from there the evolution-associated difference spectra (EADS) can be extracted (Figure 8B). The EADS map the transient spectra of all species evolving with the same dynamics. Note that the dimer excited state is the only pure spectral signature. All other components are mixtures of either the vibrationally hot and cold excited and ground state monomers and the triplet–monomer pair. The contribution of the partners to each EADS is 1:1 by mass balance. However, with no information as to the absorption coefficients of each, it is not possible to disentangle the mixed state spectra into individual components.

An approximation of how many absorbing species there were for each system (Figures S9–S14). For the quinolinone dimer, four significant SVD eigenvalues were found, and therefore a model with four absorbing species was deduced. The model used for the dimer splitting is given in Figure 7. In summary,
The computed EADS spectra display good agreement with what one would predict by empirical observation of the raw TA data. The dimer excited state (Figure 8B blue trace) shows the broad ESA feature with the dip at the region around 400 nm, which indicates possible presence of already cleaved quinolinone monomer in the singlet excited state. This in turn indicates that the initial step from dimer to the heterogeneous monomer product pair already occurs with substantial weight within the 200 fs regime. The computed inverse rate constant for this step was found to be 203 fs. Note that here we use the term heterogeneous as a reference to the differing electronic states between the two monomers formed immediately after cleavage; namely, one is in a ground singlet state, and one is in an excited singlet state. The second and third species in the EADS are the vibrationally hot and relaxed, heterogeneous monomer product pair, respectively. The EADS for these species are spectrally shifted, which is in accordance with that observed in the raw data for both the quinolinone monomer and dimer systems. The spectral shift, as stated previously, represents the process of vibrational cooling within the singlet states. For the dimer, since it is not possible to disentangle the individual contributions of the ground state and excited singlet state monomers we assume that the cooling proceeds in both monomers with the same rate. The process is estimated to occur with an inverse rate constant of 9.2 ps. Within the two monomer EADS spectra computed for the dimer data, there is also the presence of the ground state monomer absorption at the wavelength regime below 360 nm. Finally, the EADS for the triplet state is computed with good agreement to the raw data. The number obtained from the global fit, of 130 ps, is representative of the monomer singlet lifetime and not the inverse rate of intersystem crossing. Without prior knowledge of the singlet to triplet intersystem crossing quantum yield, this number cannot be deduced. However, empirical inspection of the raw data suggests that, based purely on the magnitude of the singlet and triplet signatures, the intersystem crossing yield may be on the order of 50% compared to the total singlet decay, both nonradiatively and radiatively. This would put the inverse rate of intersystem crossing on the order of twice the value computed for the singlet lifetime. The results of the global analysis for the quinolinone monomer are shown in the Supporting Information (Figures S17–19). The results were found to be in good agreement with the dimer system. The resolved EADS and the extrapolated rate constant for the vibrational relaxation within the excited monomer singlet state were found to match particularly well with that found in the dimer.

Comparison of Quinolinone Dynamics to Coumarin. The results for the quinolinone monomer and dimer species display substantial differences to that observed for the corresponding coumarin systems studied previously.49,49 To start with the monomers, the quinolinone displays more emission (≈5% fluorescence quantum yield) than the unsubstituted coumarin, which by comparison is nonemissive.49,53 The coumarin also shows no appreciable triplet yield, within the same solvent conditions, whereas the quinolinone shows substantial triplet formation. Control experiments using 7-methoxycoumarin and 7-hydroxycoumarin (umbelliferone), given in Figures S20–S21, which have the same phenyl ring functionalization making them more structurally similar to the quinolinones, were performed. The data showed that both control compounds were emissive, but no appreciable quantity of triplet ESA was observed despite the similar decay time of the S state. This indicates that the methoxy functionalization is the primary structure—function control that governs the increase in radiative quantum yield. This observation is in accordance with the literature around emissive coumarins as, e.g., laser dyes, where one of the key synthetic controls is to functionalize the coumarin with electron-donating groups at the 7-carbon position, and this is particularly effective when the electronegative functional group is amine based.53 However, the lack of triplet ESA in the control coumarins indicates that the dominating structural unit controlling the presence or absence of intersystem crossing is the lactame unit. The substitution of an oxygen to a nitrogen, as is the case when converting from a lactone to a lactame, is a simple case of altering the degree of spin–orbit coupling in organic systems that lack heavy atoms. Such phenomena is in accordance with El-Sayed’s rule.54

For the dimer cleavage, a schematic summarizing the two different pathways is given in Figure 9. Additionally, for a more physically relevant expression of the system, a Jablonski diagram has been constructed based on the all the data obtained and is shown with description in Figure S22. Coumarin dimers were found to undergo a more homogeneous ring cleavage, whereby the resulting monomer products were formed exclusively in the ground singlet state but in a vibrationally hot state with subsequent vibrational cooling. By contrast, the quinolinones display the heterogeneous pathway whereby one monomer is formed in the first excited singlet state and the other is in the ground state with a lesser degree of vibrational cooling, but it is still present. Within the experimental temporal resolution, it is not possible to unambiguously establish whether the heterogeneous mechanism found for the quinolinones is exclusive or a homogeneous
channel contributes to a small degree. To resolve this question would require that a far more quantitative experiment is needed, where the contribution of excited state monomer signal can be referenced to the total amount of initial dimer excited states formed. When factoring in the intrinsic quantum yield of dimer ring cleavage, results that deviate significantly from a ratio of 1:1 dimer signal to excited state monomer signal would indicate a mixture of heterogeneous and homogeneous ring cleavage pathways present.

**CONCLUSION**

To summarize, we have measured a new class of compounds based on the traditionally studied coumarin-based systems and found substantial changes were made to the reaction coordinate for dimer ring cleavage. Substitution of the lactone unit in classical coumarins for a lactame unit, transforming the molecule into a quinolinone framework, has been demonstrated to radically alter the photophysical properties of both monomer and dimer species. This discovery of the ability to alter the intersystem crossing yield in such a way for this class of compounds has several potential ramifications. The quinolinones were found to have intrinsically higher yields for dimerization reactions compared to the coumarin counterparts. The classic coumarin dimerization reaction is believed to proceed via the triplet state primarily due to diatomic cross-linking and solid-state polymer synthesis. For the dimers, quinolinones with their higher intrinsic yield of triplet formation could be more useful in, for example, dimer-based polymer

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.8b07186.

Fluorescence and absorption spectra used for the fluorescence quantum yield derivation, selected spectra and kinetics from the transient absorption data, singular value decomposition analysis of the data, population dynamics, nanosecond transient absorption of the quinolinones, table of excitation energies computed for the quinolinone monomer with a range of methodologies, data for the dimer cleavage quantum yield determination, structural model of the reference monomer calculated, and fs−ps transient absorption of various functionalized coumarin control molecule (PDF).

**AUTHOR INFORMATION**

*Corresponding Authors*

E-mail: hampp@uni-marburg.de.

E-mail: marcus_motzkus@pci.uni-heidelberg.de.

**ORCID**

Tiago Buckup: 0000-0002-1194-0837

Andreas Dreuw: 0000-0002-5862-5113

Norbert Hampp: 0000-0003-1614-2698

**Author Contributions**

N.P., M.J., N.H., and M.M. conceived the experiment and project. N.B. synthesized the compounds and carried out dimerization efficiency experiments. M.J., N.W., Y.L., and J.L.P.L. performed the transient absorption measurements. N.P. performed fluorescence quantum yield measurements, developed the global analysis methods, and analyzed the transient absorption data. N.P., T.B., J.L.P.L., and M.M. reviewed and discussed the data. A.D. performed the computational calculations. N.P., T.B., J.L.P.L., and M.M. reviewed and wrote the paper.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We gratefully acknowledge support by the Deutsche Forschungsgemeinschaft (DFG, Sonderforschungsbereich SFB 1249, TP B4).

**REFERENCES**


