

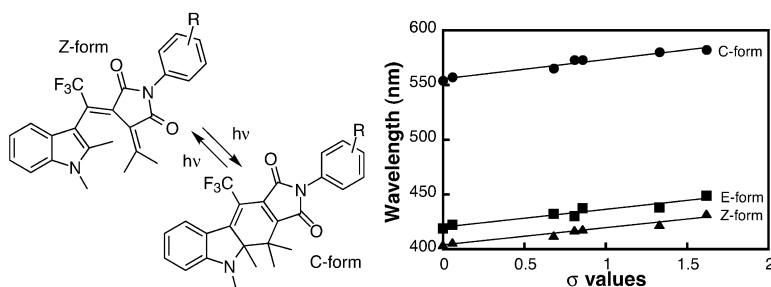
Article

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# Tuning the Optical Properties of Fluorinated Indolylfulgimides

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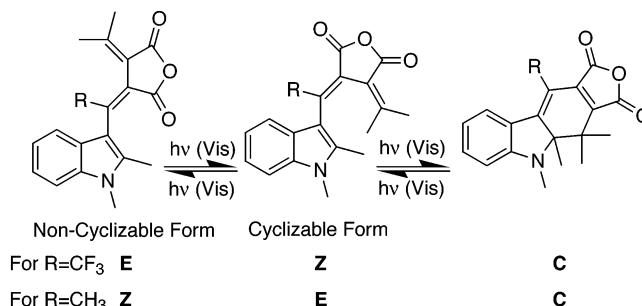
Photochromic fluorinated indolylfulgides have been identified as potential candidates for a wide range of applications including optical switches, photoregulators of biological processes, and optical memory media. In humid environments or biological systems, hydrolytic stability is essential. In an effort to improve hydrolytic stability, a series of indolylfulgimides has been synthesized from a parent trifluoromethyl-substituted indolylfulgide. The nitrogen of the succinimide moiety is linked to either a dimethyl amino or one of seven substituted phenyl groups. The phenyl groups feature substituents with increasing electron-withdrawing ability. The spectral characteristics of each compound have been examined, revealing that the wavelength absorption maxima of each form increases with increasing electron-withdrawing ability of the substituted *N*-phenyl ring. The quantum yields of the photoreactions have been determined with the *N*-(phenyl)fulgimide showing a ring closure value of nearly 0.30 in toluene. In addition, the hydrolytic, thermal, and photochemical stabilities of each compound have been measured. The fulgimides exhibit at least a 200-fold enhancement of hydrolytic stability for the *Z*-form and over a 1000-fold enhancement for the *C*-form in comparison to the same form of the parent fulgide. The *N*-(2,3,5,6-tetrafluoro-4-trifluoromethylphenyl)fulgimide can undergo up to 3000 photochemical cycles (coloration followed by bleaching) before losing 20% of its initial absorbance at photostationary state.

## Introduction

New alternatives to traditional data storage techniques are currently under development to meet the ever-increasing demands of today's information-driven society. One encouraging solution involves the use of photoactive organic materials in high-density rewriteable optical memory devices.<sup>1</sup> In such a device, the organic media would serve as the memory elements of a binary system. Photochromic organic compounds are ideal candidates for memory media because they can be interconverted between two key forms upon wavelength-specific illumination.<sup>2,3</sup> Required attributes for optical memory media include readily distinguishable absorption spectra for each form, efficient photoreactions, nondestructive read-out, and both thermal and photochemical stability. As the availability of photons generally increases with increasing wavelength, it is also desirable to utilize materials that absorb light well into the visible region.

Among the many classes of photochromic compounds, diarylethenes and fulgides have generated the greatest interest, because they meet many of the aforementioned requirements for optical memory. Within the fulgide family, indolylfulgides are particularly attractive, as they maintain the greatest resistance to photochemical and thermal stress.<sup>4</sup> Newly discovered fluorinated indolylfulgides display enhanced photochemical stability relative

## SCHEME 1. Photoreactions of Indolylfulgides<sup>a</sup>



<sup>a</sup> For fluorinated indolylfulgides, the cyclizable form is the *Z*-form (due to IUPAC nomenclature). For virtually all other fulgides the *E*- and *Z*-labels are switched.

to nonfluorinated analogues and also exhibit strong bathochromic shifts in the cyclizable *Z*-form (Scheme 1).<sup>5,6</sup> Although the thermal and photochemical stabilities of these compounds have been studied, one requirement that has been generally overlooked is hydrolytic stability.

The importance of hydrolytic stability is underscored by the fact that optical memory devices would be expected to maintain viability in humid environments. Previous studies have demonstrated that fulgides are unstable in hydrolytic solvents relative to the corresponding fulgi-

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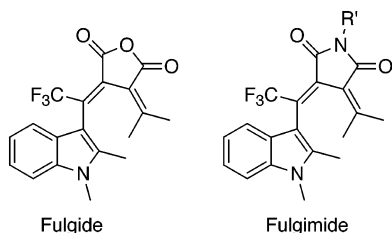
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mides.<sup>7</sup> In fulgimides, the anhydride moiety of the fulgide is replaced with an imide moiety.<sup>8</sup> Matsushima has



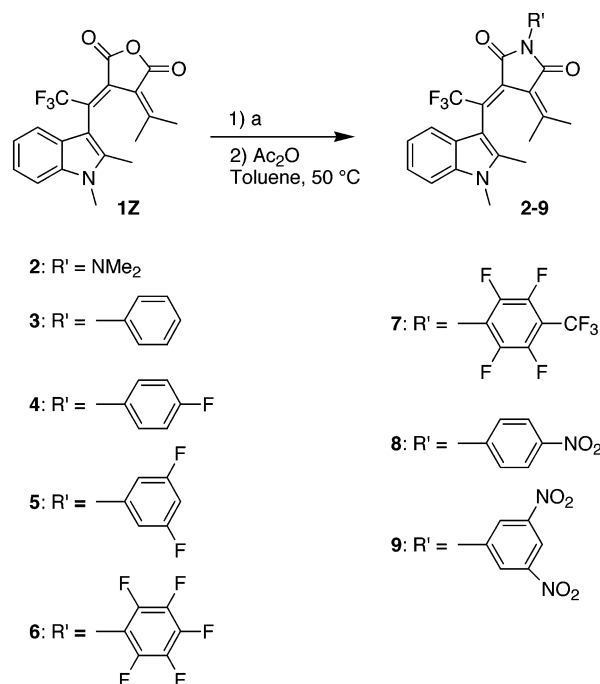
reported that the *C*-form of a thiazolylfulgide loses more than 50% of its absorbance at  $\lambda_{\max}$  after 2 days in 1:2 toluene:ethanol. In comparison, the corresponding *N*-phenyl-substituted thiazolylfulgimide did not show similar degradative loss. In addition, Matsushima has shown that fulgimides maintain photochromic activity even in aqueous mixtures (1:1 ethanol:H<sub>2</sub>O). Fulgimides have also been utilized for photoswitchable energy transfer,<sup>9,10</sup> photoregulation of binding to biomolecules,<sup>11,12</sup> and as precursors for photochromic copolymers.<sup>13,14</sup> With limited exceptions, photochemical attributes such as quantum yields and photochemical fatigue have been largely ignored.<sup>7,13,15</sup>

We have prepared a series of fluorinated indolylfulgimides using the nitrogen atom as a linker to connect substituted phenyl rings of increasing cumulative electron-withdrawing ability. It was expected that altering the electron-withdrawing ability of the phenyl ring would lend insight into the impact of electronic considerations on optical characteristics. Furthermore, we were interested in studying the hydrolytic stability of fulgimides in aqueous solutions as prior reports featured limited characterization. Herein, we report the photochemical attributes of a series of fulgimides including predictive trends in absorption spectra and the quantum yields of the coloration (ring closing) and bleaching (ring opening) photoreactions. In addition, each compound has been analyzed for its thermal, photochemical, and hydrolytic stability.

## Results and Discussion

**Synthesis.** Trifluoromethyl-substituted indolylfulgide **1Z** was prepared as previously reported.<sup>16</sup> Fulgide **1Z** then served as a precursor to fluorinated indolylfulgimides **2–9** (Scheme 2). Anhydride ring opening of **1Z** via

## Scheme 2<sup>a</sup>



<sup>a</sup> Reagents: (a) for **2** and **3**, NH<sub>2</sub>R', THF, 60 °C; for **4–7**, NH<sub>2</sub>R', NaH, toluene, 50 °C; for **8** and **9**, NH<sub>2</sub>R', LDA, DMF.

**TABLE 1.** Extinction Coefficients at  $\lambda_{\max}$  for Fulgide **1** and Fulgimides **2–9** in Toluene

compd	$\lambda_{\max}/\text{nm}$ ( $\epsilon_{\max}/\text{mol}^{-1} \text{ L cm}^{-1}$ )		
	<i>Z</i> -form	<i>E</i> -form	<i>C</i> -form
<b>1</b>	427 (5300)	441 (5600)	571 (6400)
<b>2</b>	399 (5500)	395 (5700)	545 (6500)
<b>3</b>	404 (5800)	419 (6000)	554 (6900)
<b>4</b>	406 (6400)	422 (6100)	557 (7400)
<b>5</b>	412 (6500)	432 (5600)	565 (7300)
<b>6</b>	418 (5500)	437 (4300)	573 (6500)
<b>7</b>	422 (5800)	438 (6000)	580 (6800)
<b>8</b>	417 (6600)	430 (5700)	573 (7700)
<b>9</b>	432 (6100)	449 (6400)	582 (7700)

addition of 1,1-dimethylhydrazine or substituted anilines generated the corresponding *N*-substituted succinamic acid.<sup>17</sup> To enhance reactivity, anilines substituted with electron-withdrawing groups were deprotonated with NaH or LDA prior to the addition of **1Z**. Subsequent dehydration of the succinamic acid intermediates with acetic anhydride in toluene yielded indolylfulgimides **2–9**. All of the fulgimides were obtained as crystals in the *Z*-form. However, on occasion, compounds **5** and **6** crystallized exclusively in the *E*-form.

**Optical Characteristics.** The extinction coefficients and absorption maxima of each form of fulgimides **2–9** are shown in Table 1. With the exception of compound **9**, each fulgimide experienced a hypsochromic shift in its *Z*-form absorption spectra relative to parent fulgide **1Z**. With regard to the *C*-form spectra, fulgimides **6–9** displayed moderate bathochromic shifts relative to fulgide **1C**. With the exception of *N*-(dimethylamino)fulgimide **2**, the noncyclizable *E*-form of each compound had a longer wavelength maximum than the cyclizable *Z*-form.

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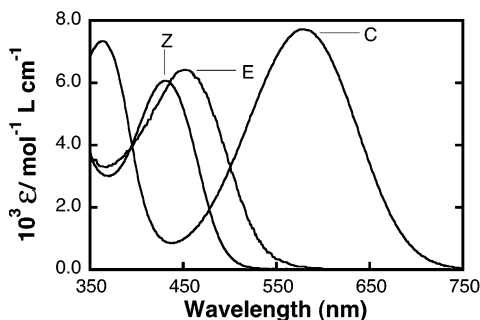
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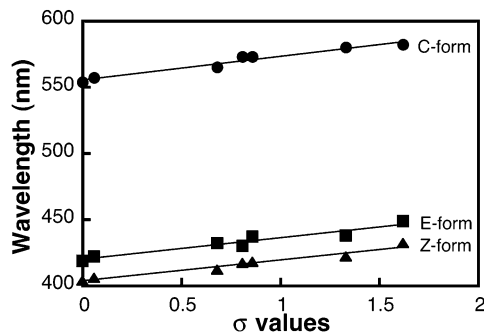
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**FIGURE 1.** Absorption spectra of the *Z*-, *E*-, and *C*-forms of dinitro-substituted indolylfulgimide **9** in toluene.



**FIGURE 2.** Hammett plot of wavelength maxima vs  $\sigma$  value for all three forms of fulgimides **3–9**. In order of increasing  $\sigma$  values: **3** (0.0), **4** (0.06), **5** (0.68), **8** (0.81), **6** (0.86), **7** (1.32), **9** (1.62).

As the cumulative electron-withdrawing power of the phenyl-substituents increased, there was a corresponding increase in the *Z*-form wavelength absorption maxima. A similar trend was also observed for the *E*- and *C*-forms of each compound. The trend culminates with the *Z*-form of dinitro-substituted fulgimide **9** displaying the longest wavelength maxima for any fulgimide reported to date (Figure 1).

The electron-withdrawing ability of the substituted phenyl ring of fulgimides **3–9** was quantified by summation of the known  $\sigma$  values for each substituent.<sup>18</sup> In the case of ortho substitution, the  $\sigma$  value corresponding to para substitution was utilized. A plot of the sum of the  $\sigma$  values vs the wavelength maxima of the *Z*-, *E*-, and *C*-forms revealed correlation coefficients of  $>0.95$  for each form (Figure 2). The linear curve fits yielded the following equations:

$$\text{Z-form: } Y = 404 \text{ nm} + 15.8\Sigma(\sigma) \text{ nm}$$

$$\text{E-form: } Y = 420 \text{ nm} + 16.4\Sigma(\sigma) \text{ nm}$$

$$\text{C-form: } Y = 556 \text{ nm} + 17.7\Sigma(\sigma) \text{ nm}$$

It should be noted that the Rentzepis group has synthesized<sup>19</sup> and optically characterized a limited number of *N*-phenyl-substituted 2-indolylfulgimides that reveal similar trends, thus suggesting that these correlations may be somewhat general. Matsushima et al.

**TABLE 2.** Quantum Yields of Photoreactions for Fulgide **1** and Fulgimides **2–9** in Toluene

compd	irradiation at 427 nm				irradiation at 559 nm	
	$\Phi_{ZC}$	$\Phi_{CZ}$	$\Phi_{ZE}$	$\Phi_{EZ}$	$\Phi_{CZ}$	C:Z:E at PSS <sub>427nm</sub>
<b>1</b>	0.20	0.10	0.014	0.022	0.043	95:3:2
<b>2</b>	0.28	0.16			0.069	91:8:1
<b>3</b>	0.29	0.11			0.070	93:6:1
<b>4</b>	0.22	0.15			0.060	93:6:1
<b>5</b>	0.23	0.17	0.005	0.021	0.057	93:6:1
<b>6</b>	0.28	0.14	0.013	0.026	0.046	94:4:2
<b>7</b>	0.27	0.21			0.044	94:5:1
<b>8</b>	0.23	0.07			0.045	96:3:1
<b>9</b>	0.25	0.09			0.039	92:5:3

did not observe this trend when measuring absorption spectra of furylfulgimides at the photostationary state (PSS). However, due to the possible presence of other forms, the wavelength absorption maxima measured at PSS may not represent the true absorption maxima of the pure compound. The ability to tailor the wavelength absorption maxima of phenyl-substituted fluorinated indolylfulgimides represents an advancement in the field of photochromics. One could envision the preparation of new indolylfulgimides with predictable absorptive characteristics designed and optimized for specific applications.

**Quantum Yields.** Measurement of the quantum yields for ring closure ( $\Phi_{ZC}$ ) and ring opening ( $\Phi_{CZ}$ ) was carried out as previously described.<sup>5</sup> In keeping with former studies, initiation of ring closure was accomplished via irradiation with  $\lambda = 427$ -nm light, while the ring opening reactions were probed with  $\lambda = 559$ -nm light.<sup>6</sup>

Few examples exist comparing the photochromic properties of fulgimides to their parent fulgides. Smets reports little to no difference in quantum yield between the two species for either ring closing or ring opening.<sup>15</sup> Rentzepis reports a moderate decrease in the quantum yield of ring opening in a nonpolar solvent (hexane), while a much larger loss in efficiency is seen for ring closing.<sup>13</sup> In the case of the fulgimides detailed herein, compounds **2–9** all displayed greater ring closing quantum yields in toluene than the parent trifluoromethyl-substituted indolylfulgide **1**. Phenyl-substituted fulgimide **3** showed the largest quantum yield with a value of 0.29, nearly 50% higher than the fulgide precursor. The values obtained for  $\Phi_{ZC}$  for the series of fulgimides yielded no apparent trend with increasing electron-withdrawing substituents on the phenyl ring (Table 2).

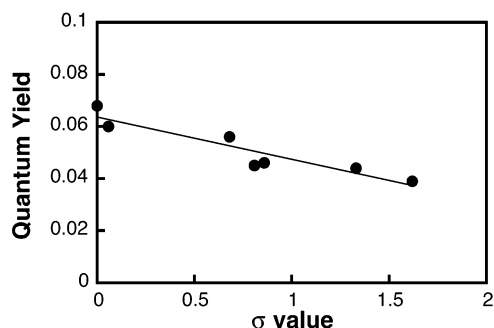
The ring-opening photoreactions did reveal a common trend, as the quantum yield decreased with the increasing additive electron-withdrawing nature of the substituted phenyl ring. As a result, the lowest ring opening quantum yield exists for the dinitrophenyl-substituted fulgimide **9**. A Hammett plot of  $\Phi_{CZ}$  vs  $\sigma$  value for compounds **3–9** showed reasonable correlation, with  $R = 0.93$  (Figure 3).

The excellent separation of the UV–vis spectra of the cyclizable *Z*-form and the ring-closed *C*-form results in outstanding control of the photoreactions of coloration and bleaching. In all cases, the photostationary state derived from irradiation with  $\lambda = 427$  nm (PSS<sub>427nm</sub>) contained at least 90% *C*-form (Table 2). Ring-opening quantum yields at 427 nm ( $\Phi_{CZ427nm}$ ) have been deter-

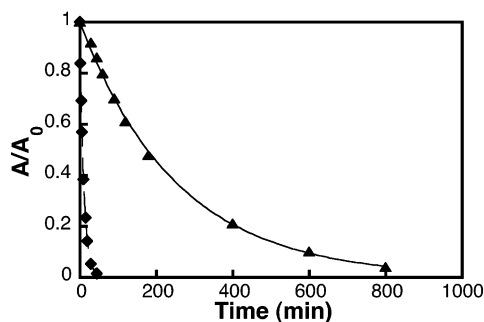
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**FIGURE 3.** Hammett plot of  $\Phi_{CZ}$  vs  $\sigma$  value for fulgimides **3–9**. The Y-axis format is identical to the one shown in Figure 2.

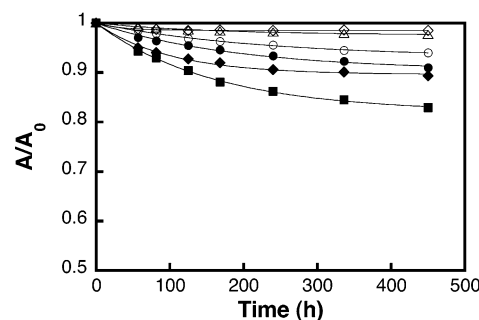


**FIGURE 4.** Loss of absorbance with time for indolylfulgide **1Z** (triangles) and **1C** (diamonds) in 70:30 EtOH:H<sub>2</sub>O at room temperature. Rate constants for hydrolysis were fitted to exponential decay:  $k_C = 9.51 \times 10^{-2} \text{ min}^{-1}$ ,  $k_Z = 3.94 \times 10^{-3} \text{ min}^{-1}$ .

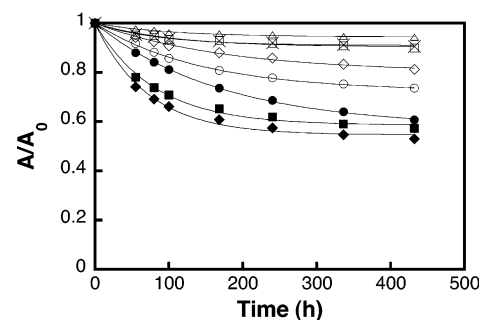
mined from the photostationary state compositions (Table 2). The *C*-form present in the PSS<sub>427nm</sub> can be quantitatively converted to the *Z*-form with  $\lambda = 559\text{-nm}$  irradiation, as the *Z*-forms maintain no absorbance above 530 nm.

**Hydrolytic Stability.** A notable disadvantage of most fulgides is their relative instability under humid or moist conditions. It has been demonstrated that the anhydride moiety is highly susceptible to hydrolysis.<sup>7</sup> Both the *Z*- and *C*-forms of fluorinated indolylfulgide **1** displayed rapid loss of absorbance at room temperature when dissolved in a 70:30 ethanol:H<sub>2</sub>O mixture (Figure 4). The composition of the ethanol:H<sub>2</sub>O mixture was dictated by solubility concerns; higher percentages of water resulted in precipitation of the fulgimide from solution. Cyclic fulgide **1C** was fully consumed within 45 min, and irradiation of the resulting solution with 430-nm light yielded no changes in the UV-vis spectra. No evidence existed to support *C* to *Z* isomerization under the given reaction conditions. Although fulgide **1Z** displayed greater resistance to hydrolysis than its cyclic counterpart **1C**, it only took 12 h to fully degrade.

In contrast, fluorinated indolylfulgimides **2–9** displayed far superior resistance to hydrolysis (Figures 5 and 6). With the exception of *N*-(nitrophenyl)fulgimide **8**, the *Z*-forms maintained at least 90% of their absorbance at  $\lambda_{\text{max}}$  after 2 weeks at room temperature in 70:30 ethanol:H<sub>2</sub>O (Table 3). Furthermore, fulgimides **2** and **4** showed no decomposition within experimental error. In general, the *Z*-forms of fulgimides **7–9** featuring trifluoromethyl or nitro substituents on the phenyl ring



**FIGURE 5.** Hydrolytic decomposition of the *Z*-forms of fulgimides **3** and **5–9** in 70:30 EtOH:H<sub>2</sub>O: open triangles (**3**), open circles (**5**), open diamonds (**6**), filled circles (**7**), filled squares (**8**), filled diamonds (**9**). The rates of decomposition were determined by fitting the curves to  $y = (1 - A)e^{-kt}$ .



**FIGURE 6.** Hydrolytic decomposition of the *C*-form of fulgimides **2–9** in 70:30 EtOH:H<sub>2</sub>O: open squares (**2**), open triangles (**3**), crosses (**4**), open circles (**5**), open diamonds (**6**), filled circles (**7**), filled squares (**8**), filled diamonds (**9**). The rates of decomposition were determined by fitting the curves to  $y = (1 - A)e^{-kt}$ .

**TABLE 3.** Hydrolytic Stability of Fluorinated Indolylfulgides after 336 h at 22 °C in 70:30 EtOH:H<sub>2</sub>O

compd	$A/A_0^a$		compd	$A/A_0^a$	
	<i>Z</i> -form	<i>C</i> -form		<i>Z</i> -form	<i>C</i> -form
<b>1</b>		b	<b>6</b>	0.986	0.833
<b>2</b>	c	0.909	<b>7</b>	0.923	0.641
<b>3</b>	0.979	0.946	<b>8</b>	0.845	0.591
<b>4</b>	c	0.913	<b>9</b>	0.901	0.547
<b>5</b>	0.945	0.753			

<sup>a</sup> Absorbance at  $\lambda_{\text{max}}$  relative to initial absorbance after 336 h at room temperature. <sup>b</sup> Both forms of fulgide **1** decomposed fully within 12 h. <sup>c</sup> No loss of absorbance within experimental error.

degraded faster than the fluoro-containing compounds. No clear trend emerged for the hydrolytic stability of fulgimides **3–6**.

Concurrent *C*-to-*Z* isomerization complicated measurement of the hydrolytic stability of the *C*-forms of fulgimides **2–9**. The values obtained for the *C*-forms represent an upper limit to the rate of hydrolytic degradation, because loss of absorbance occurred through both hydrolysis and isomerization to the *Z*-forms. Still, each compound maintained at least 55% of its original absorbance at the *C*-form  $\lambda_{\text{max}}$  after 2 weeks at room temperature in 70:30 ethanol:H<sub>2</sub>O. The loss in absorbance increased with increasing electron-withdrawing ability of the substituents on the phenyl ring. The only exception to this rule was the *N*-(difluorophenyl)fulgimide **5**, which degraded faster than pentafluoro-substituted analogue **6**.

**TABLE 4. Thermal Stability of Fluorinated Indolylfulgimides in PMMA at 80 °C**

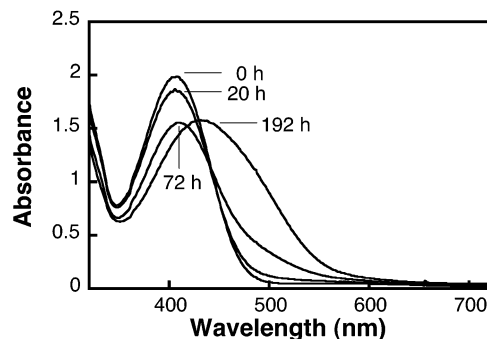
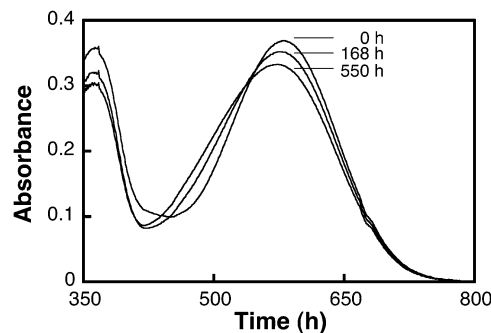
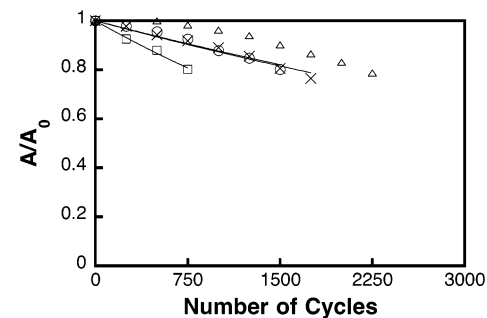
compd	$A/A_0$		compd	$A/A_0$	
	Z-form <sup>a</sup>	C-form <sup>b</sup>		Z-form <sup>a</sup>	C-form <sup>b</sup>
<b>1</b>	0.550	0.920	<b>6</b>	0.869	0.903
<b>2</b>	0.921	0.974	<b>7</b>	0.860	0.897
<b>3</b>	0.940	c	<b>8</b>	0.891	0.975
<b>4</b>	0.897	0.891	<b>9</b>	0.871	0.927
<b>5</b>	0.884	0.979			

<sup>a</sup> Absorbance at  $\lambda_{\max}$  relative to initial absorbance after 20 h at 80 °C. <sup>b</sup> Absorbance at  $\lambda_{\max}$  relative to initial absorbance after 550 h at 80 °C. <sup>c</sup> No loss of absorbance within experimental error.

The relative hydrolytic stability of the fulgides and fulgimides will depend on the definition of stability, as fulgides decompose exponentially and fulgimides do not. However, the most conservative comparison, that of the initial rates of hydrolysis, can be made. For fulgides, the initial rate is  $k$ , while for fulgimides, it is  $(1 - A)k$  (Figures 4–6). On the basis of initial rates, the C-forms of the fulgimides are 3–4 orders of magnitude more stable and the Z-forms are at least 200-fold more stable than the corresponding fulgide form. For all compounds, the C-form was less stable in aqueous environments than the Z-form and thus likely to be the most vulnerable to hydrolytic degradation in most applications.

**Thermal Stability.** Materials intended for use in optical memory devices must maintain viability at elevated temperatures for extended periods of time. Current industry standards such as CD and archival tapes purport to maintain stability up to 50 °C. The thermal stability of both the Z- and C-forms of fulgimides **2–9** was measured in poly(methyl methacrylate) (PMMA) films held at 80 °C (Table 4). The temperature of 80 °C was chosen to allow direct comparison to previously studied fulgides, including compound **1Z**. Previous studies have demonstrated the relative instability of indolylfulgide **1** toward thermal stress.<sup>5</sup> Indeed, the Z-form of **1** lost nearly half of its absorbance at  $\lambda_{\max}$  after only 20 h at 80 °C. Each of the derivatives examined herein displayed greater thermal stability in the Z-form, highlighted by phenyl-substituted fulgimide **2**, which lost only 6.0% of its absorbance under identical conditions. It should be noted that despite the slower degradation exhibited by the fulgimides, a similar pattern emerged in the time-dependent UV–vis scans. For each compound, an initial drop in absorbance is followed by a bathochromic shift and subsequent increase in absorbance (Figure 7). Judging by the similarities between the shifts in the UV–vis spectra, it can be postulated that the Z-forms of the fulgimides undergo the same degradative pathway that has been established for fulgide **1Z**, albeit at a slower rate.<sup>20</sup>

Table 4 also shows the outstanding thermal stability of the C-forms of fulgimides **2–9**. After 1 week at 80 °C, each compound maintained at least 94% of its initial absorbance. Fulgimides **3** and **5** showed no loss of absorption within experimental error after 1 week. The C-forms of each fulgimide retained at least 89% of its initial absorbance even after 3 weeks at elevated temperature. Figure 8 shows the change in the absorption

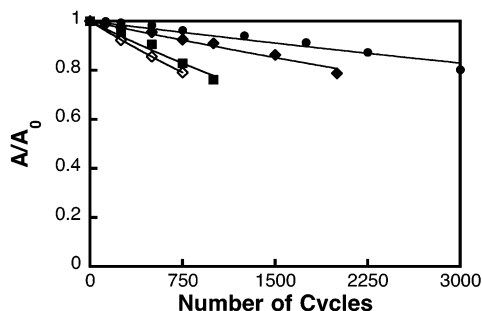
**FIGURE 7.** Thermal degradation of phenyl-substituted indolylfulgimide **3** in PMMA.**FIGURE 8.** Thermal degradation of pentafluorophenyl-substituted indolylfulgimide **6** in PMMA.**FIGURE 9.** Photochemical decomposition of **2–5** in toluene, giving decreasing absorbance with repeated coloration and bleaching cycles: open squares (**2**), open triangles (**3**), crosses (**4**), open circles (**5**). The decomposition of compounds **2**, **4**, and **5** was fit to an exponential decay.

spectra of indolylfulgimide **6** in PMMA with prolonged exposure to 80 °C.

**Photochemical Stability.** The repeatability of the photochemical coloration and bleaching of fluorinated fulgimides **2–9** was measured in toluene using a method similar to one previously detailed.<sup>5</sup> Ring closure was initiated with  $\lambda = 410$ -nm light, while ring opening was achieved with  $\lambda > 530$ -nm light. Samples were irradiated to 90% of the photostationary state (PSS<sub>410nm</sub>) attained for ring closure, followed by quantitative bleaching as described by Irie.<sup>21</sup> Data were fit to an exponential decay to determine percent decomposition per photochemical cycle (Figures 9 and 10). No photodecomposition products were isolated in the study.

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(21) Irie, M. *Chem. Rev. (Washington, D. C.)* **2000**, *100*, 1685–1716.

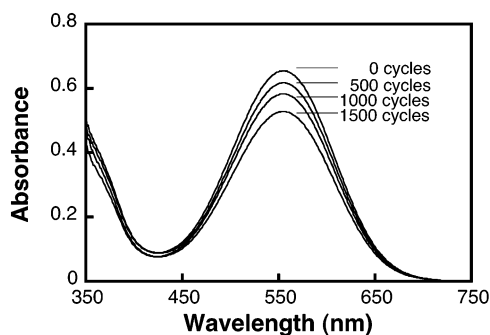


**FIGURE 10.** Photochemical decomposition of **6–9** in toluene, giving decreasing absorbance with repeated coloration and bleaching cycles: open diamonds (**6**), filled circles (**7**), filled squares (**8**), filled diamonds (**9**). Decomposition of compounds **6–9** was fit to an exponential decay.

**TABLE 5. Photochemical Fatigue Resistance of Fulgide 1 and Fulgimides 2–9 in Toluene**

compd	no. of cycles <sup>a</sup>	$A/A_0$	%/cycle	compd	no. of cycles <sup>a</sup>	$A/A_0$	%/cycle
<b>1</b>	3000 <sup>b</sup>	0.791	0.007	<b>6</b>	750	0.791	0.031
<b>2</b>	750	0.801	0.028	<b>7</b>	3000	0.802	0.006
<b>3</b>	2250	0.786	c	<b>8</b>	750	0.828	0.025
<b>4</b>	1500	0.805	0.014	<b>9</b>	2000	0.788	0.011
<b>5</b>	1500	0.801	0.013				

<sup>a</sup> Number of photochemical cycles attained at 20% loss of absorbance of the PSS. <sup>b</sup> Photochemical fatigue of fulgide **1** was measured with 436-nm light. <sup>c</sup> Photochemical decomposition of *N*-(phenyl)fulgimide **3** could not be fitted to exponential decay.



**FIGURE 11.** Photostationary state absorbances of fulgimide **4** in toluene after the indicated number of cycles.

In general, indolyl-substituted fulgides are more photochemically robust than fulgides containing other aromatic groups.<sup>4,22</sup> Additionally, fluorination of the methyl group attached to the bridging alkene of indolylfulgides has been shown to provide an enhancement in photochemical fatigue resistance relative to the nonfluorinated analogue.<sup>6</sup> Although the fulgimide derivatives maintain strong resistance to photochemical degradation, a majority of the compounds failed to match the stability of parent trifluoromethyl fulgide **1** (Table 5).<sup>5</sup> The single exception was fulgimide **7**, highlighted by a degradation rate of only 0.006% per cycle. No correlation could be drawn between the percentage decomposition per cycle and the electronic structure of the substituted phenyl rings of **3–9**. Figure 11 shows the absorption spectrum of fulgimide **4** as a function of photoconversion in intervals of 500 photocycles.

A curious anomaly to the exponential-like photochemical decay was provided by phenyl-substituted fulgimide **3** (Figure 9). For the first 500 cycles, the compound reproducibly displayed no loss of absorbance at PSS<sub>410nm</sub> within experimental error. As the number of cycles increased, the rate of degradation increased rapidly, suggesting an autocatalytic mechanism. At this point, the pathway of photochemical degradation remains unclear.

## Conclusion

Fluorinated indolylfulgimides **2–9** display several attractive characteristics in comparison to parent indolylfulgide **1**. Areas of particular interest include enhanced hydrolytic stability, improvement of the ring-closing quantum yields, and tunable absorption spectra. For the most part, the thermal and photochemical stability of the fluorinated indolylfulgimides remains comparable to the parent fulgide. Fulgimide **7** loses only 0.006% of its absorbance per photochemical cycle, making it the most photochemically robust fulgide derivative reported to date.

We have demonstrated that the *Z*- and *C*-forms of fulgimides **2–9** are at least 200- to 1000-fold more stable respectively in aqueous environments than the same form of fulgide **1**. The *Z*-forms of fulgimides **2** and **4** showed no loss in absorbance within experimental error after 2 weeks in 70:30 ethanol:H<sub>2</sub>O. With the augmented hydrolytic stability, fulgimides display potential for utilization in a variety of environments. Hydrolytic stability is vital for addressing biological concerns such as photo-regulation of enzymatic activity.<sup>11,23,24</sup> In addition, fulgimides used in optical memory devices are not expected to show degradative loss under humid conditions.

Furthermore, the use of substituted phenyl groups linked to the nitrogen of the succinimide functionality affords materials with finely tuned spectral characteristics. Increasing the cumulative electron-withdrawing ability of the phenyl ring results in predictive bathochromic shifts for the *Z*, *E*, and *C*-form spectra. Accordingly, dinitro-substituted fulgimide **9** has the longest *Z*-form absorption maxima of any fulgimide reported to date. Future compounds can be rationally designed making use of the predictive model presented herein.

## Experimental Section

**General Procedures and Materials.** All commercially available materials were used without further purification. NMR spectra were recorded on a 300 MHz NMR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR samples were internally referenced to TMS (0.00 ppm). Flash chromatography was performed with 230–400 mesh silica gel. E&R Microanalytical Laboratory Inc. performed all elemental analysis.

The *C*-forms of compounds **2–9** were obtained by irradiating *Z*-form solutions with 427-nm light followed by purification via flash column chromatography (silica gel:toluene). The resulting pure *C*-form solutions were utilized directly for spectra determination. Fulgimides **2–9** were initially prepared in the *Z*-form. The *E*-forms of compounds **5** and **6** were also isolated upon separate crystallization.

**Preparation of Fulgimides 2 and 3 (2 Given as Representative).** To a stirred solution of **1Z** (151 mg, 0.42 mmol)

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in THF (40 mL) was added 1,1-dimethylhydrazine (500  $\mu$ L, 6.6 mmol). The solution was heated to 60 °C and stirred until the color was lost (approximately 5 min). Solvent was removed in vacuo and the resulting solid was suspended in toluene (40 mL). Upon addition of 5 mL of acetic anhydride, the solid immediately dissolved and the solution was tinted orange. The solution was allowed to stir at 70 °C for 10 min and solvent was removed in vacuo to yield an orange oil. Purification via column chromatography (2:1 hexane:ethyl acetate) and crystallization from 4:1 hexane:dichloromethane yielded *N*-(dimethylamino)fulgimide as a yellow solid (33.5 mg, 20% yield).

***N*-(Dimethylamino)fulgimide (2).** *Z*-Form: 20% yield;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.30–7.09 (m, 4H), 3.70 (s, 3H), 3.02 (s, 6H), 2.21 (s, 3H), 2.11 (s, 3H), 0.92 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  165.8, 164.2, 153.7, 136.9, 136.7, 131.8, 125.4, 122.4 (q,  $J_{\text{CF}} = 278$  Hz), 121.9, 121.5, 121.3, 120.9, 119.5, 109.1, 107.2, 44.4, 30.0, 26.4, 22.2, 11.9. Anal. Calcd for  $\text{C}_{21}\text{H}_{22}\text{F}_3\text{N}_3\text{O}_2$ : C, 62.21; H, 5.47; F, 14.06; N, 10.36. Found: C, 62.08; H, 5.54; F, 14.42; N, 10.35. *C*-Form:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 8.4$  Hz, 1H), 7.35 (t,  $J = 8.4$  Hz, 1H), 6.78 (t,  $J = 8.4$  Hz, 1H), 6.62 (d,  $J = 8.4$  Hz, 1H), 2.93 (s, 6H), 2.91 (s, 3H), 1.78 (s, 3H), 1.32 (s, 3H), 1.23 (s, 3H).

***N*-(Phenyl)fulgimide (3).** *Z*-Form: 27% yield;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.54–7.37 (m, 5H), 7.34–7.13 (m, 4H), 3.72 (s, 3H), 2.28 (s, 3H), 2.16 (s, 3H), 1.00 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  166.3, 164.1, 154.5, 137.1, 136.8, 132.7, 131.6, 129.3 (q,  $J_{\text{CCF}} = 36$  Hz), 128.9, 128.3, 126.8, 125.4, 122.6, 122.5 ( $J_{\text{CF}} = 277$  Hz), 121.9, 120.9, 119.6, 109.2, 107.6, 29.9, 26.6, 22.4, 12.0. Anal. Calcd for  $\text{C}_{25}\text{H}_{21}\text{F}_3\text{N}_2\text{O}_2$ : C, 68.49; H, 4.83; F, 13.00; N, 6.39. Found: C, 68.17; H, 4.67; F, 12.71; N, 6.06. *C*-Form:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 8.1$  Hz, 1H), 7.49–7.43 (m, 2H), 7.39–7.32 (m, 4H), 6.79 (t,  $J = 7.2$  Hz, 1H), 6.65 (d,  $J = 8.1$  Hz, 1H), 2.95 (s, 3H), 1.84 (s, 3H), 1.39 (s, 3H), 1.30 (s, 3H).

**Preparation of Fulgimides 4–7 (4 Given as Representative).** To a solution of **1Z** (147 mg, 0.40 mmol) with suspended magnesium sulfate (250 mg) in toluene (40 mL) was added 4-fluoroaniline (230 mg, 2.1 mmol). The solution was allowed to stir for 10 min at 50 °C. Sodium hydride (75 mg, 1.9 mmol; 60% dispersion in oil) was added and the solution allowed to stir for 4 h at 50 °C. To the now colorless solution was added 25 mL of acetic anhydride. The solution immediately turned orange and was allowed to stir for an additional 30 min at 50 °C. Precipitates were then filtered off, and the solvent was removed in vacuo to yield an orange solid. Purification via flash chromatography ( $\text{CH}_2\text{Cl}_2$ ) and crystallization from ligroin and dichloromethane provided *N*-(4-fluorophenyl)fulgimide as bright orange crystals (65.8 mg, 36% yield).

***N*-(4-Fluorophenyl)fulgimide (4).** *Z*-Form: 36% yield;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.49–7.37 (m, 2H), 7.35–7.13 (m, 6H), 3.72 (s, 3H), 2.28 (s, 3H), 2.15 (s, 3H), 1.00 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  166.2, 164.0, 162.0 (d,  $J_{\text{CF}} = 249$  Hz), 154.7, 137.0, 136.8, 132.3, 129.8, 128.7, 128.6, 127.5, 125.3, 122.5, 122.4 (q,  $J_{\text{CF}} = 278$  Hz), 120.9, 119.6, 115.9 (d,  $J_{\text{CCF}} = 24$  Hz), 109.2, 107.8, 30.0, 26.7, 22.4, 12.0. Anal. Calcd for  $\text{C}_{25}\text{H}_{20}\text{F}_4\text{N}_2\text{O}_2$ : C, 65.79; H, 4.42; F, 16.65; N, 6.14. Found: C, 66.01; H, 4.38; F, 16.98; N, 5.93. *C*-Form:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 8.4$  Hz, 1H), 7.40–7.33 (m, 3H), 7.17–7.11 (m, 2H), 6.80 (t,  $J = 7.5$  Hz, 1H), 6.65 (d,  $J = 8.4$  Hz, 1H), 2.95 (s, 3H), 1.83 (s, 3H), 1.38 (s, 3H), 1.29 (s, 3H).

***N*-(3,5-Difluorophenyl)fulgimide (5).** *Z*-Form: 11% yield;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.35–7.11 (m, 6H), 6.92–6.82 (m, 1H), 3.71 (s, 3H), 2.28 (s, 3H), 2.16 (s, 3H), 1.01 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  165.5, 163.4, 162.7 (dd,  $J_{\text{CF}} = 249$  Hz,  $J_{\text{CCF}} = 14$  Hz), 155.8, 137.3, 136.8, 133.4 (t,  $J_{\text{CCF}} = 14$  Hz), 131.5, 130.4 (q,  $J_{\text{CF}} = 35$  Hz), 125.2, 122.4 (q,  $J_{\text{CF}} = 278$  Hz), 122.1, 121.0, 119.5, 110.3, 110.2 (d,  $J_{\text{CCF}} = 27$  Hz), 110.1, 109.3, 103.8 (t,  $J_{\text{CCF}} = 25$  Hz), 30.0, 26.8, 22.6, 12.1. Anal. Calcd for  $\text{C}_{25}\text{H}_{19}\text{F}_5\text{N}_2\text{O}_2$ : C, 63.29; H, 4.04; F, 20.02; N, 5.90. Found: C, 63.36; H, 3.94; F, 20.39; N, 5.78. *E*-Form:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 7.8$  Hz, 1H), 7.30 (d,  $J = 7.8$  Hz, 1H), 7.20 (m, 1H), 7.12 (m, 1H), 6.91 (m, 2H), 6.75 (m, 1H), 3.74 (s, 3H), 2.52 (s, 3H), 2.38 (s,

3H), 2.30 (q,  $J = 1.5$  Hz, 3H). *C*-Form:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 6.9$  Hz, 1H), 7.38 (t,  $J = 8.4$  Hz, 1H), 7.12–7.04 (m, 2H), 6.83–6.76 (m, 2H), 6.66 (d,  $J = 8.4$  Hz, 1H), 2.95 (s, 3H), 1.83 (s, 3H), 1.38 (s, 3H), 1.29 (s, 3H).

***N*-(2,3,4,5,6-Pentafluorophenyl)fulgimide (6).** *Z*-Form: 53% yield;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.35–7.13 (m, 4H), 3.72 (s, 3H), 2.28 (s, 3H), 2.16 (s, 3H), 1.04 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  164.2, 162.0, 157.3, 145.7 (m), 143.9 (dm,  $J_{\text{CF}} = 259$  Hz), 142.1 (dm,  $J_{\text{CF}} = 257$  Hz), 138.0 (dm,  $J_{\text{CF}} = 253$  Hz), 137.4, 136.9, 131.3 (q,  $J_{\text{CCF}} = 36$  Hz), 131.0, 125.1, 122.2, 122.2 (q,  $J_{\text{CF}} = 278$  Hz), 122.0, 121.2, 119.5, 109.3, 107.4, 30.1, 26.9, 22.7, 12.0. Anal. Calcd for  $\text{C}_{25}\text{H}_{16}\text{F}_8\text{N}_2\text{O}_2$ : C, 56.83; H, 3.05; F, 28.76; N, 5.30. Found: C, 56.96; H, 3.06; F, 29.04; N, 5.25. *E*-Form:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 7.8$  Hz, 1H), 7.29 (d,  $J = 7.8$  Hz, 1H), 7.19 (m, 1H), 7.12 (m, 1H), 3.73 (s, 3H), 2.52 (s, 3H), 2.37 (s, 3H), 2.32 (q,  $J = 1.5$  Hz, 3H). *C*-Form:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 7.8$  Hz, 1H), 7.39 (t,  $J = 7.8$  Hz, 1H), 6.81 (t,  $J = 8.1$  Hz, 1H), 6.66 (d,  $J = 8.1$  Hz, 1H), 2.96 (s, 3H), 1.82 (s, 3H), 1.40 (s, 3H), 1.31 (s, 3H).

***N*-(2,3,5,6-Tetrafluoro-4-trifluoromethylphenyl)fulgimide (7).** *Z*-Form: 64% yield;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.34–7.14 (m, 4H), 3.73 (s, 3H), 2.29 (s, 3H), 2.17 (s, 3H), 1.06 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  163.6, 161.4, 157.8, 145.1 (m), 144.8 (dm,  $J_{\text{CF}} = 245$  Hz), 143.8 (dm,  $J_{\text{CF}} = 254$  Hz), 137.5, 136.9, 131.7 (q,  $J_{\text{CCF}} = 36$  Hz), 130.6, 125.0, 122.3, 122.1 (q,  $J_{\text{CF}} = 278$  Hz), 121.5, 121.3, 120.5 (q,  $J_{\text{CF}} = 266$  Hz), 119.5, 115.5, 109.4, 107.3, 30.1, 26.9, 22.8, 12.0. Anal. Calcd for  $\text{C}_{26}\text{H}_{16}\text{F}_{10}\text{N}_2\text{O}_2$ : C, 53.99; H, 2.79; F, 32.85; N, 4.84. Found: C, 54.29; H, 3.00; F, 32.85; N, 4.64. *C*-Form:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 8.4$  Hz, 1H), 7.40 (t,  $J = 8.4$  Hz, 1H), 6.81 (t,  $J = 8.4$  Hz, 1H), 6.67 (d,  $J = 8.4$  Hz, 1H), 2.97 (s, 3H), 1.83 (s, 3H), 1.42 (s, 3H), 1.31 (s, 3H).

**Preparation of Fulgimides 8 and 9 (8 Given as Representative).** To a stirred solution of **1Z** (175 mg, 0.48 mmol) in DMF (30 mL) at 0 °C was added 4-nitroaniline (80 mg, 0.58 mmol). LDA (0.5 mL, 2.0 M solution) was added and the solution immediately turned red. After 14 h at room temperature the solvent was removed in vacuo and the resulting solid was suspended in toluene (10 mL). Acetic anhydride (5 mL) was then added and the resulting orange solution was allowed to stir at room temperature for 1 h before the solvent was removed in vacuo. Purification via flash chromatography (2:1 hexane:ethyl acetate) and crystallization from 2-propanol provided *N*-(4-nitrophenyl)fulgimide as bright orange crystals (89 mg, 38% yield).

***N*-(4-Nitrophenyl)fulgimide (8).** *Z*-Form: 38% yield;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.39–8.32 (m, 2H), 7.79–7.72 (m, 2H), 7.34–7.14 (m, 4H), 3.72 (s, 3H), 2.30 (s, 3H), 2.16 (s, 3H), 1.02 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  165.4, 163.4, 156.3, 146.6, 137.4, 137.3, 136.8, 131.3, 130.3 (q,  $J_{\text{CCF}} = 32$  Hz), 127.2, 125.1, 124.1, 122.1, 122.3 (q,  $J_{\text{CF}} = 276$  Hz), 122.0, 121.1, 119.5, 109.3, 107.4, 30.1, 26.8, 22.7, 12.2. Anal. Calcd for  $\text{C}_{25}\text{H}_{20}\text{F}_3\text{N}_3\text{O}_4$ : C, 62.11; H, 4.17; F, 11.79; N, 8.69. Found: C, 61.88; H, 4.27; F, 11.94; N, 8.51. *C*-Form:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.15 (d,  $J = 9.0$  Hz, 2H), 7.77 (d,  $J = 8.4$  Hz, 1H), 7.71 (d,  $J = 9.0$  Hz, 2H), 7.39 (t,  $J = 7.8$  Hz, 1H), 6.82 (t,  $J = 7.8$  Hz, 1H), 6.67 (d,  $J = 8.4$  Hz, 1H), 2.97 (s, 3H), 1.85 (s, 3H), 1.40 (s, 3H), 1.30 (s, 3H).

***N*-(2,4-Dinitrophenyl)fulgimide (9).** *Z*-Form: 17% yield;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  9.00 (d,  $J = 2.3$  Hz, 1H), 8.59 (dd,  $J = 8.7$ , 2.3 Hz, 1H), 7.85 (d,  $J = 8.7$  Hz, 1H), 7.80–7.48 (m, 4H), 3.72 (s, 3H), 2.32 (s, 3H), 2.17 (s, 3H), 1.06 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  164.6, 162.3, 157.7, 147.1, 145.4, 137.7, 136.9, 131.8, 131.4, 130.8, 127.9, 125.5, 122.2 (q,  $J_{\text{CF}} = 278$  Hz), 122.1, 121.8, 121.3, 119.7, 109.3, 107.5, 30.1, 27.2, 22.8, 11.7. Anal. Calcd for  $\text{C}_{25}\text{H}_{19}\text{F}_3\text{N}_4\text{O}_6$ : C, 56.82; H, 3.62; F, 10.79; N, 10.60. Found: C, 56.58; H, 3.57; F, 10.67; N, 10.43. *C*-Form:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.98 (d,  $J = 2.4$  Hz, 1H), 8.59 (dd,  $J = 9.0$ , 2.4 Hz, 1H), 7.76 (d,  $J = 9.0$  Hz, 2H), 7.40 (t,  $J = 8.1$  Hz, 1H), 6.82 (t,  $J = 8.1$  Hz, 1H), 6.67 (d,  $J = 8.1$  Hz, 1H), 2.97 (s, 3H), 1.81 (s, 3H), 1.45 (s, 3H), 1.31 (s, 3H).

**Preparation of Thin Films.** An initial solution was prepared by adding 2–4 mg of fulgimide to a solution of 10%



poly(methyl methacrylate) (PMMA, low molecular weight, average  $M_w$  ca. 120 000) in  $\text{CH}_2\text{Cl}_2$  (5 mL). The polymer solution (1.5 mL) was then deposited via pipet onto circular 1 in.  $\times$   $1/16$  in. BK-7 glass slides (escoproducts) and allowed to spread over the surface of the slide. The sample was allowed to dry overnight at room temperature. The resulting films varied in thickness from 100 to 200  $\mu\text{m}$  and were utilized in the thermal stability studies.

**Spectra Determination.** Concentrated, air-saturated stock solutions of the *Z*-form of fulgimides **2–9** and the *E*-form of fulgimides **5** and **6** in toluene were prepared in duplicate or triplicate. From each stock solution, five samples ranging in concentration from 0.20 to 0.05 mM were then prepared by dilution with toluene. Absorption coefficients and  $\lambda_{\text{max}}$  were determined. *E*-form spectra for compounds **2–4** and **7–9** were obtained via spectral subtraction of an *E/Z* mixture in toluene- $d_8$  generated by irradiation with 350-nm light and bleached with 580-nm light to eliminate *C*-form. The relative concentrations of the *E*- and *Z*-forms were determined via  $^1\text{H}$  NMR.

Stock solutions containing freshly purified *C*-form in toluene (see General Procedures and Materials) were diluted to four or five different concentrations and their UV–vis spectra obtained. Each *C*-form solution was then quantitatively converted to *Z*-form with 580-nm light and the concentration of fulgimide present was ascertained using the predetermined *Z*-form extinction coefficients. Absorption coefficients and  $\lambda_{\text{max}}$  for the *C*-forms were then determined from the initial spectra.

**Quantum Yields.** Quantum yields for ring closing ( $\Phi_{\text{ZC}}$ ) and *E*-to-*Z* photoisomerization reactions ( $\Phi_{\text{EZ}}$ ) were determined with monochromatic light of wavelength 427 nm. Quantum yields for ring-opening reactions ( $\Phi_{\text{CZ}}$ ) were determined with monochromatic light of wavelength 559 nm. Determination of quantum yields for the *Z*-to-*E* photoreaction ( $\Phi_{\text{ZE}}$ ) is detailed in the following section. A Coherent Infinity XPO laser served as the radiation source for all quantum yield experiments.

Air-saturated solutions of fulgimides **2–9** were prepared in toluene with an approximate concentration of 0.1 mM. Samples were irradiated to between 5 and 10% conversion as determined by HPLC and UV–vis. Coherent LMP-2 energy detectors measured the amount of light absorbed by the fulgimide solution in comparison to a toluene blank. Separation of isomers for the coloration and bleaching reactions was achieved using a Waters Spherisorb S5 W column with toluene as the eluent at a flow rate of 4.0 mL/min. Separation of isomers for the *E*-to-*Z* photoisomerization reaction was achieved using the same column with 85:15 hexane:dioxane as the eluent at a flow rate of 2.7 mL/min. The apparatus was calibrated with the chemical actinometer trioxalatoferate(III) and Aberchrome 540, a furylfulgide.

**Photostationary State Measurements.** Fulgimides **2–9** were irradiated with 427-nm light supplied by a Coherent Infinity XPO laser and their isomeric ratios monitored via HPLC until a photostationary state ( $\text{PSS}_{427\text{nm}}$ ) was attained.

The isomers were separated using a Waters Spherisorb S5 W column with 85:15 hexane:dioxane as the eluent at a flow rate of 2.7 mL/min. A 1:1:1 mixture of the three isomers in toluene was analyzed via HPLC to ascertain their relative extinction coefficients in the HPLC solvent. Where applicable, quantum yields for  $\Phi_{\text{ZE}}$  and  $\Phi_{\text{CZ}}$  at 427 nm were determined from the photostationary state measurements.

**Photochemical Stability.** Air-saturated solutions of the *Z*-form of fulgimides **2–9** were prepared in toluene with an initial absorbance of 0.6 at the absorption maxima. Samples were irradiated to the photostationary state with light supplied from an Oriel 200 W Hg(Xe) lamp utilizing a 410-nm narrow band-pass filter. After measuring the UV–vis spectra of the  $\text{PSS}_{410\text{nm}}$  mixture, a pure *Z*-form solution was irradiated to 90% of the PSS and the reaction was timed. The 90% PSS mixture was then bleached with >530-nm light using a separate filter and again the reaction was timed. Absorbance at the *C*-form  $\lambda_{\text{max}}$  was <0.01 upon bleaching.

Once the duration of irradiation was established for both the 90% PSS coloration and <1% *C*-form bleaching reactions, the system was automated through use of a filter switch. All solutions were capped and stirred. Control experiments were performed to correct for evaporation. After a designated number of irradiation cycles, the samples were fully converted to  $\text{PSS}_{410\text{nm}}$  and their UV–vis spectra scanned. The photochemical fatigue was then determined by comparison with the initial  $\text{PSS}_{410\text{nm}}$  absorption spectrum.

**Thermal Stability.** Thin films containing either the *Z*- or *C*-form of fulgimides **2–9** were wrapped in aluminum foil and placed in an oven maintained at 80  $^\circ\text{C}$ . The films were removed at prescribed intervals and their UV–vis spectra measured. The films were monitored for the shorter of 10 d or until no further changes occurred in the UV–vis spectra.

**Hydrolytic Stability.** Solutions of approximately 0.1 mM concentration of both the *Z*- and *C*-forms of fulgide **1** and fulgimides **2–9** were prepared in a 70:30 ethanol: $\text{H}_2\text{O}$  mixture. Samples were transferred to 3.0 mL stoppered cuvettes and wrapped in Teflon tape and Parafilm to prevent evaporative loss. Initial UV–vis spectra were obtained and solutions were then placed in the dark. At prescribed intervals, the solutions were removed and their UV–vis spectra scanned. Samples were monitored for loss of absorbance for the shorter of 450 h or until fully decomposed.

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