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Optical and thermal properties of photochromic fluorinated adamantylidene indolylfulgides

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Abstract

Fluorinated indolylfulgides are a class of photochromic organic compounds with potential applications in the areas of optical memory and optical switches. Absorption spectra, quantum yields, and thermal stability have been measured for a series of fluorinated adamantylidene indolylfulgides. The cyclizable form of the trifluoromethyl-substituted 5-methoxy-1,2-dimethylindolylfulgide displays the longest absorbance maxima reported for the fulgide family. The thermal stability of the cyclizable form of the fluorinated adamantylidene indolylfulgides was greater than that of their corresponding fluorinated isopropylidene analogs, as expected based upon the mechanism of decomposition for isopropylidene analogs. The pentafluoroethyl-substituted adamantylidene indolylfulgide showed only a 27% loss in absorbance after 5 weeks at 80 °C in a poly(methylmethacrylate) film. These studies have highlighted the rational design of a thermally stable cyclizable form for fluorinated indolylfulgides. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photochromism; Fulgide; Stability; Fluorination; 3D optical storage; Optical switches

1. Introduction

Photochromic organic compounds that undergo reversible color changes upon illumination have long been viewed as potential media for inclusion in high-density optical memory devices [1,2]. Two such classes of photochromic compounds that have been extensively investigated are diarylethenes [3] and fulgides [4]. Among the various heterocyclic fulgides, indolyl-substituted fulgides are noted for a bathochromic shift of the non-cyclized forms and improved photochemical fatigue resistance (Scheme 1) [5,6]. Recently, a new class of fluorinated indolylfulgides has demonstrated enhanced coloration quantum yields, more pronounced bathochromic shifts of the non-cyclized forms, and greater photochemical stability [7,8]. Unfortunately, the cyclizable form of these new compounds was shown to degrade rapidly in both solution [9] and polymer films [8] upon prolonged exposure to elevated temperatures.

Mechanistic studies have aided in the identification of the decomposition pathway for **1***Z* and lent further insight into the preparation of a more thermally stable *Z*-form fluorinated indolylfulgide. Scheme 2 illustrates the thermal rearrangement of **1***Z* to **3***E* via intermediate **2**. Isolation of key intermediate **2** provided evidence for an initial 1,5-sigmatropic hydrogen shift followed by a formal indolyl migration [9]. In an effort to block the initial hydrogen shift, which originates from the methyl on the isopropylidene (IPP) unit of **1***Z*, we have prepared a series of admantylidene (ADD) substituted fulgides **4–7** (Scheme 3). It was expected that hydrogen migration from the corresponding adamantylidene would be impeded, as the resulting intermediate would possess a disallowed bridgehead double bond and thus be in violation of Bredt's rule (Scheme 4). Methoxy-indole-substituted isopropylidene fulgide **8** was prepared to provide a comparison to adamantylidene fulgide **7**. Herein, we report optical properties such as absorption spectra, wavelength maxima, extinction coefficients, and coloration and bleaching quantum yields for each compound. In addition, we detail thermal stability in poly(methylmethacrylate) (PMMA) for both the *Z*- and *C*-form fulgides within the series, along with a solution-based study for adamantylidene fulgide **4**.

2. Experimental details

2.1. Materials

2.1.1. Synthesis

Fulgides **4–6** were prepared as previously reported [10], while fulgides **7** and **8** were obtained following the same general procedure. Generation of the methoxy-substituted

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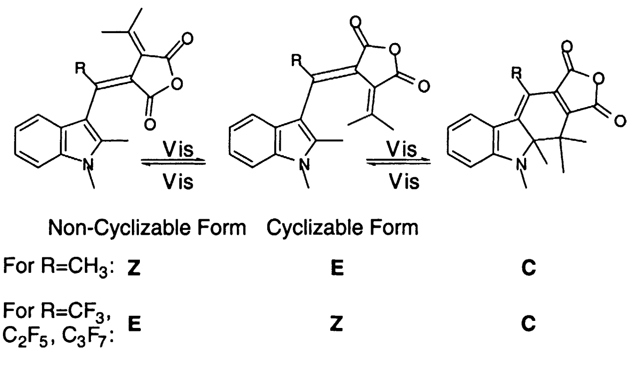
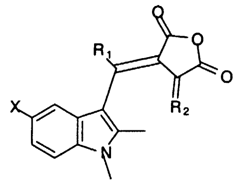
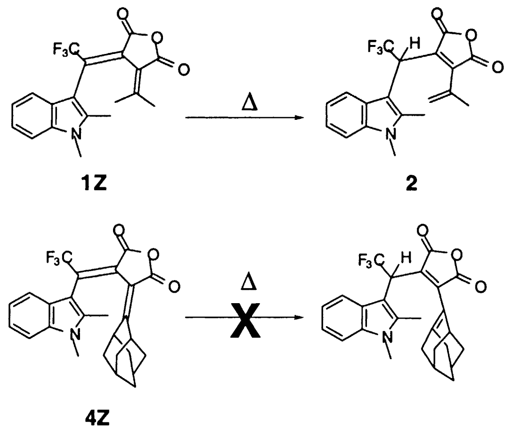


Scheme 1. Photochemical reactions of indolylfulgides. For fluorinated indolylfuglides, the cyclizable form is the *Z*-form (due to IUPAC nomenclature). For virtually all other fulgides, the *E*-form is the cyclizable form.



Fulgide	R_1	R_2	X
4	CF_3	ADD	H
5	C_2F_5	ADD	H
6	C_3F_7	ADD	H
7	CF_3	ADD	OMe
8	CF_3	IPP	OMe

Scheme 3. Indolylfulgides **4**–**8**.



Scheme 4. Thermal rearrangement of adamantylidene indolylfulgide 4*Z* via 1,5-hydrogen shift would result in a bridgehead double bond and thus be in violation of Bredt's rule.

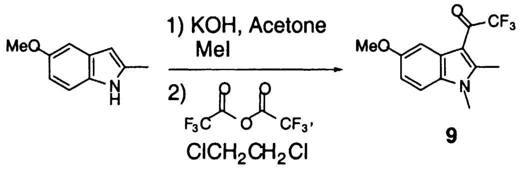
indole precursor **9** proceeded smoothly via *N*-alkylation of 5-methoxy-2-methylindole followed by acetylation with trifluoroacetic anhydride (Scheme 5) [11]. All ^{1}H NMR spectra were acquired on a Bruker 300 MHz NMR spectrometer and internally referenced to $CHCl_3$ at 7.26 ppm.

3-Trifluoroacetyl-5-methoxy-1,2-dimethyl indole (**9**) (81% from 5-methoxy-2-methylindole): ^{1}H NMR ($CDCl_3$) δ 7.58 (d, $J_{\mathrm{HH}} = 2.0$ Hz, 1H), 7.19 (d, $J_{\mathrm{HH}} = 8.9$ Hz, 1H), 6.91 (dd, $J_{\mathrm{HH}} = 8.9$ Hz, $J_{\mathrm{HH}} = 2.0$ Hz, 1H), 3.87 (s, 3H), 3.67 (s, 3H), 2.71 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 174.9 (q, $J_{\mathrm{CCF}} = 36$ Hz), 156.7, 149.5, 131.8, 126.3, 117.2 (q, $J_{\mathrm{CF}} = 289$ Hz), 112.5, 110.4, 107.8, 103.7 (q, $J_{\mathrm{CCCF}} = 4$ Hz), 55.7, 30.1, 13.1. Anal. Calcd. for $C_{13}H_{12}F_3NO_2$: C, 57.57; H, 4.46; F, 21.01; N, 5.16. Found: C, 57.86; H, 4.36; F, 20.71; N, 5.05.

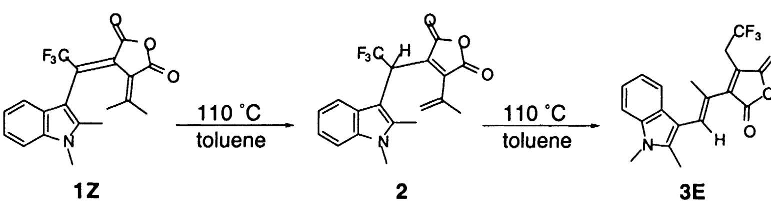
Subsequent Stobbe condensation of **9** with either diethyl isopropylidene or adamantylidene succinate produced a corresponding mixture of *cis* and *trans* indolelactones, **10**. Lactone ring-opening with NaH in DMF followed by addition of water yielded isopropylidene and adamantylidene diacids, **11**, which were cleanly converted to fulgides **7** and **8** when treated with acetic anhydride (Scheme 6).

7*Z* (36% from **9**): ^{1}H NMR ($CDCl_3$) δ 7.20 (d, $J_{\mathrm{HH}} = 8.8$ Hz, 1H), 6.91 (s, 1H), 6.88 (dd, $J_{\mathrm{HH}} = 8.8$ Hz, $J_{\mathrm{HH}} = 2.4$ Hz, 1H), 4.28 (s, 1H), 3.82 (s, 3H), 3.71 (s, 3H), 3.08 (s, 1H), 2.31 (s, 3H), 2.15–1.89 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 178.5, 161.7, 160.6, 155.7, 132.3, 130.5 (q, $J_{\mathrm{CCF}} = 32$ Hz), 132.2 (q, $J_{\mathrm{CF}} = 277$ Hz), 113.8, 112.3, 111.5, 111.4, 110.3, 109.9, 104.0, 102.4, 55.7, 41.3, 40.6, 39.1, 38.9, 38.1, 36.4, 34.3, 30.3, 27.4, 27.1, 11.4. Anal. Calcd. for $C_{27}H_{26}F_3NO_4$: C, 66.80; H, 5.40; F, 11.74; N, 2.80. Found: C, 67.05; H, 5.47; F, 11.69; N, 2.86.

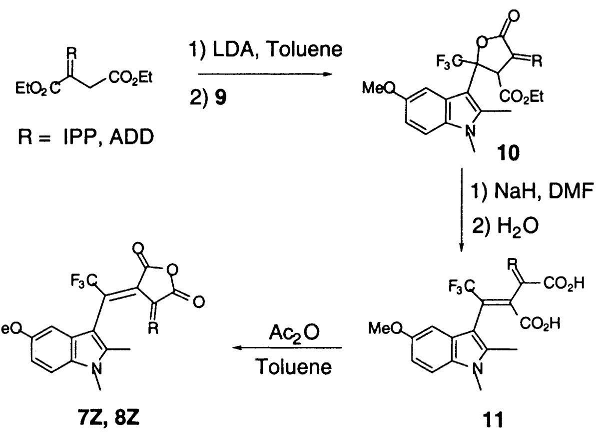
8*Z* (36% from **9**): ^{1}H NMR ($CDCl_3$) δ 7.18 (d, $J_{\mathrm{HH}} = 8.9$ Hz, 1H), 6.87 (dd, $J_{\mathrm{HH}} = 8.9$ Hz, $J_{\mathrm{HH}} = 2.4$, 1H), 6.57 (d, $J_{\mathrm{HH}} = 2.4$ Hz, 1H), 3.79 (s, 3H), 3.68 (s, 3H), 2.27 (s, 3H) 2.18 (s, 3H), 0.98 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 161.9, 160.4, 159.8, 155.2, 138.4, 132.6 (q, $J_{\mathrm{CCF}} = 35$ Hz), 131.9, 127.3, 125.0, 122.0 (q, $J_{\mathrm{CF}} = 278$ Hz), 120.4, 112.3, 110.4, 106.7, 101.4, 55.7, 30.2, 26.6, 23.2, 12.3. Anal. Calcd. for $C_{20}H_{18}F_3NO_4$: C, 61.38; H, 4.89; F, 14.72; N, 3.56. Found: C, 61.07; H, 4.61; F, 14.49; N, 3.56.



Scheme 5.



Scheme 2. Thermal decomposition of fluorinated indolylfulgide 1*Z*.



Scheme 6.

All fulgides were initially prepared in the *Z*-form. Generation of *C*-form fulgides proceeded via irradiation of the *Z*-form in toluene with 427 nm light supplied by a Coherent Infinity XPO laser. The solutions were then purified by flash column chromatography (toluene as eluent on silica gel); purity was confirmed by a Hitachi D-7000 HPLC using a Waters Spherisorb S5 W column with 85:15 hexane:dioxane as the eluent at a flow rate of 2.5 ml/min. The resulting *C*-form solutions were used directly for spectroscopic measurements.

2.1.2. Thin films

Thin films were prepared as reported previously [8].

2.2. Spectroscopic measurements

Concentrated, air-saturated stock solutions of the *Z*-form of fulgides **4–8** in toluene were prepared in duplicate or triplicate. From each stock solution, 4 or 5 samples ranging in concentration from 0.20 to 0.05 mM were then prepared by dilution with toluene. Absorption coefficients and λ_{max} were determined using a Cary 1 spectrophotometer. *E*-form spectra were obtained via spectral subtraction of an *E*/*Z* mixture in toluene-d_8 generated by irradiation with 350 nm light. The solution was bleached with 580 nm light to eliminate *C*-form fulgide and the relative concentration of *E*- and *Z*-form was determined via ^{1}H NMR.

Freshly purified *C*-forms were diluted 4 or 5 times and spectra were obtained with a Cary 1 spectrophotometer. Each *C*-form solution was quantitatively converted to *Z*-form with 580 nm light and the concentration of fulgide present was ascertained using the predetermined *Z*-form extinction coefficients. Absorption coefficients and λ_{max} for the *C*-forms were then determined from the initial spectra.

2.3. Photochemical properties

Quantum yields and photostationary state measurements at 427 nm were determined as reported previously [8].

2.4. Thermal stability

2.4.1. Polymer studies

Thin films containing either *Z*- or *C*-form of fulgides **4–8** were wrapped in aluminum foil and placed in an oven maintained at 80 °C. The films were removed at prescribed intervals and their UV–Vis spectra were scanned on a Cary 1 spectrophotometer. The *Z*-form films were monitored for 5 weeks or until no further change occurred in the UV–Vis spectra. *C*-form films of fulgides **4–7** were monitored until complete thermal reversion to *Z*-form occurred.

2.4.2. Solution studies

A 9.0 mM solution of **4***Z* and 5-methoxy-2-methylindole (equimolar internal standard) was prepared in toluene-d_8. The solution was divided into 0.80 ml portions, each of which were transferred to an ampule. Ampules were then sealed under vacuum and submersed in a constant temperature bath at 80 °C. At prescribed times an ampule was removed and its contents were analyzed by ^{1}H NMR.

3. Results and discussion

3.1. UV–Vis absorption spectra

Fluorinated adamantylidene indolylfulgides **4–6** display similar spectra to the corresponding isopropylidene fulgides [8], and the absorption maxima for the *Z*-, *E*- and *C*-forms are presented in Table 1. Extinction coefficients were only slightly lowered as a consequence of the adamantyl

Table 1
Quantum yields and extinction coefficients at λ_{max} for fulgides **4–8** in toluene

Fulgide	λ_{max}/nm (ε_{max}/(mol^{-1} l cm^{-1}))			427 (nm)		559 (nm), Φ_{CZ}	*C*:*Z*:*E* at PSS$_{427\,nm}$
	Z-form	*E*-form	*C*-form	Φ_{ZC}	Φ_{CZ}		
4	426 (4800)	442 (7500)	571 (5400)	0.051	0.153	0.325	84:11:5
5	431 (4000)	445 (5600)	588 (5500)	0.034	0.124	0.326	80:14:6
6	433 (3900)	450 (5500)	589 (5400)	0.040	–[a]	0.319	63:37[a]
7	435 (5200)	450 (7900)	615 (6000)	0.030	0.326	0.166	40:34:26
8	433 (6100)	449 (7200)	616 (7200)	0.169	0.046	0.012	94:3:3

[a] Unable to separate the *Z*- and *E*-forms via HPLC.

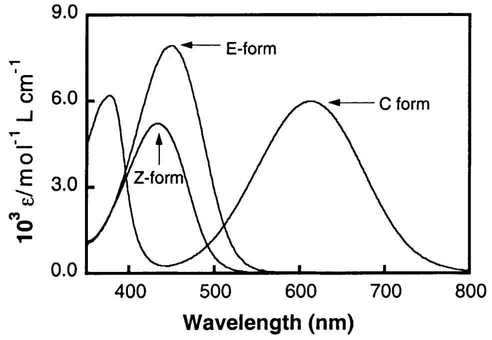


Fig. 1. UV–Vis absorption spectra for fulgide **7** in toluene.

group. The absorption maxima of the *Z*- and *E*-forms exhibited greater than 40 nm bathochromic shift relative to the corresponding non-fluorinated adamantylidene analogs [12]. As was expected based on literature precedence, fulgides **7** and **8** containing the 5-methoxy-1,2-dimethyl indole moiety experienced a modest bathochromic shift in the cyclizable *Z*-form and a large shift in the *C*-form due to the electron donating ability of the methoxy substituent [13,14]. The excitation maxima of methoxy-indole-substituted adamantylidene fulgide **7** (435 nm) matches the longest yet reported for the cyclizable isomer of the fulgide family (Fig. 1).

3.2. Quantum yields

Measurement of coloration (ϕ_{ZC}) and bleaching (ϕ_{CZ}) quantum yields for fulgides **4**–**8** was accomplished as detailed previously [8]. In accordance with earlier reports for non-fluorinated counterparts, adamantylidene substitution affected lowered coloration quantum yields [15] relative to isopropylidene-substituted fulgides (Table 1). In addition, the increased steric bulk results in a profound sixfold to eightfold enhancement of the quantum yields for the bleaching reactions. Augmentation of the ring-opening quantum yield is presumably due to the increased strain on the central cyclohexadiene ring of the *C*-form. Fulgides **7** and **8** containing the 5-methoxy-substituted indole showed decreased bleaching quantum yields due to stabilization of the *C*-form via electron donation through the conjugated system. Comparison of fulgides **7** and **8** shows in striking detail the impact of sterics on quantum yields; adamantylidene substitution results in a more than 12-fold increase in bleaching efficiency and a sixfold decrease in coloration efficiency.

Additionally, adamantylidene substitution results in a decrease in the percentage conversion to *C*-form upon photostationary state irradiation with 427 nm light ($\mathrm{PSS}_{427\,\mathrm{nm}}$). Previously fluorinated indolylfulgides have attained as high as 95% conversion at $\mathrm{PSS}_{427\,\mathrm{nm}}$. Due to modest *C*-form absorption and large ϕ_{CZ} at 427 nm, none of the adamantylidene fulgides studied achieve more than 84% conversion to *C*-form. A noteworthy example of this phenomenon is methoxy-substituted adamantylidene fulgide **7**, which has a ϕ_{CZ} of 0.326 at 427 nm, accounting for its minimal 40% conversion to *C*-form upon photostationary state irradiation. Conversely, isopropylidene analog **8** reaches 94% conversion as ring-opening with 427 nm light is significantly retarded ($\phi_{CZ} = 0.046$ at 427 nm).

Table 2
Thermal resistivity of *Z*-form fulgides **4**–**8** at 80 °C in PMMA film

Fulgide	*Z*-form thermal decomposition[a]		
	A/A_0 (17.5 h)	A/A_0 (72 h)	A/A_0 (840 h)
4	0.93	0.87	0.57
5	0.98	0.92	0.73
6	0.86	0.73	0.36
7	0.85	0.72	0.33
8	–[b]	–[b]	–[b]

[a] A/A_0 refers to the absorbance relative to the initial value at the maximum wavelength for the indicated isomer at 80 °C after the denoted time.

[b] Methoxy-indole-substituted isopropylidene fulgide **8** displayed a 40% loss in absorbance after 6 h. By 17.5 h, the material had undergone a 20 nm shift in $\lambda_{\max}$ and the absorbance had increased.

3.3. Thermal stability

To test the thermal stability of the *Z*-forms, PMMA thin films doped with fulgides **4**–**8** were heated to 80 °C. The temperature of 80 °C was chosen to allow comparison to previous studies [5,7–9]. After 17.5 h, pentafluoroethyl adamantylidene fulgide **5** experienced a modest 2% decrease in absorbance at the *Z*-form $\lambda_{\max}$ (Table 2). In comparison, the isopropylidene analog of **5** displayed a 44% decrease in absorbance after the same time period [8]. Overall, fulgide **5** exhibited the highest *Z*-form thermal stability, retaining 73% of its absorbance after a remarkable 840 h (5 weeks) at 80 °C (Fig. 2). Irradiation of these thin films demonstrated the continued existence of photochromic activity. Although the *Z*-forms of adamantylidene fulgides **6** and **7** are less thermally stable than **4** and **5**, they nonetheless resist thermal stress far more effectively than their isopropylidene analogs. Methoxy substitution on the indole portion of the fulgide resulted in an increased rate of thermal decomposition, particularly with regard to isopropylidene

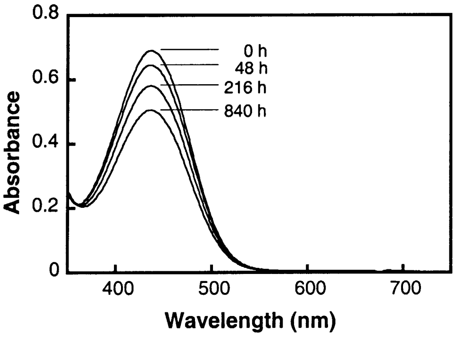


Fig. 2. UV–Vis absorption spectra of **5***Z* in PMMA with continuing treatment at 80 °C.

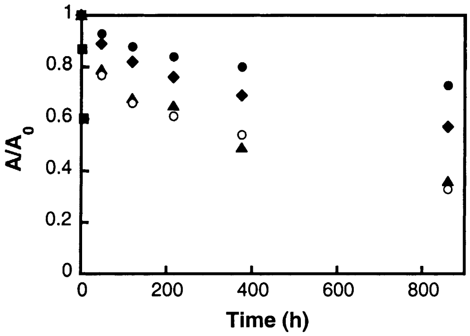


Fig. 3. Thermal decomposition of *Z*-form fulgides **4–8** in PMMA; decreasing absorbance upon treatment at 80 °C: diamonds (**4**), filled circles (**5**), triangles (**6**), open circles (**7**) and squares (**8**).

fulgide **8**, which degrades even faster than its non-methoxy-substituted analog.

Fig. 3 depicts the thermal stability of *Z*-form fulgides **4–8** in terms of loss of absorbance versus time when held at 80 °C. It should be noted that the adamantylidene fulgides experienced no change in absorption maxima upon degradation, whereas isopropylidene counterparts show an initial loss in absorbance followed by a red shift and subsequent increase in absorbance. In an attempt to identify a thermolysis product, trifluoromethyl adamantylidene fulgide **4***Z* was heated to 80 °C in toluene-d_8 and ^{1}H NMR spectra were examined at prescribed intervals. The solution-based study displayed minor *Z*- to *E*-form thermal isomerization up to 168 h, but no new peaks attributable to thermal decomposition products.

Not surprisingly, the *C*-forms of the fulgides **4–7** undergo thermal reversion upon heating [15]. The *C*-form of fulgide **4** loses 73% of its absorbance at $\lambda_{\max}$ after 24 h at 80 °C; **5–7** display complete reversion over the same interval. Fig. 4 demonstrates the thermal decomposition of **5***C* to **5***Z* over the course of 16 h. Presence of an isosbestic point suggests that the reaction does not proceed via a stable intermediate. Methoxy-substituted isopropylidene fulgide **8***C* displays comparable thermal stability to other *C*-form isopropylidene fulgides and does not undergo reversion to the cyclizable *Z*-form (Fig. 5).

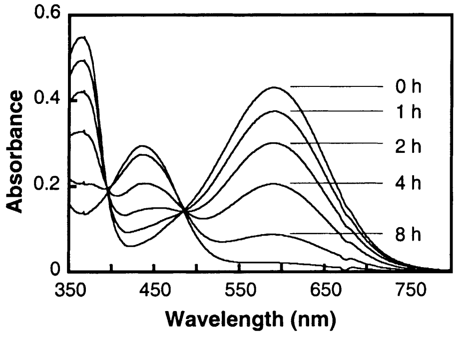


Fig. 4. UV–Vis spectra illustrating the ring-opening of **5***C* to **5***Z* in PMMA upon exposure to 80 °C.

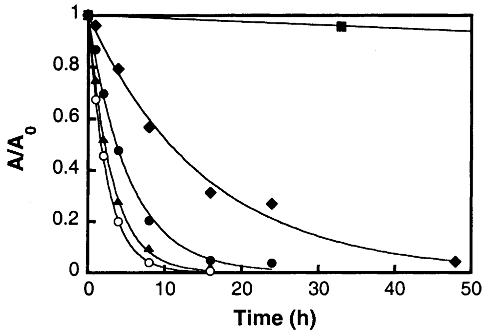


Fig. 5. Thermal decomposition of *C*-form fulgides **4–8** in PMMA; decreasing absorbance upon treatment at 80 °C: diamonds (**4**), filled circles (**5**), triangles (**6**), open circles (**7**) and squares (**8**). Rate constants were obtained by fitting the data to a first-order decay: $k_4 = 1.1 \times 10^{-3}\ \text{min}^{-1}$, $k_5 = 3.1 \times 10^{-3}\ \text{min}^{-1}$, $k_6 = 5.2 \times 10^{-3}\ \text{min}^{-1}$, $k_7 = 6.6 \times 10^{-3}\ \text{min}^{-1}$.

4. Conclusion

Fluorinated indolylfulgides have many favorable properties making them potentially useful for a number of applications including optical switches and optical memory. Fluorinated adamantylidene indolylfulgides feature a large red shift in $\lambda_{\max}$ for the *Z*- and *E*-forms relative to their non-fluorinated adamantylidene analogs. In a similar fashion to their non-fluorinated analogs the *C*-forms undergo thermal reversion to the cyclizable form. Although there is little variation in electronic absorption spectra between fluorinated adamantylidene and isopropylidene indolylfulgides, there exists a dramatic difference in quantum yields for both ring-closure (ϕ_{ZC}) and ring-opening (ϕ_{CZ}). A stunning enhancement is noted for the thermal stability of *Z*-form fluorinated adamantylidene indolylfulgides in comparison to fluorinated isopropylidene indolylfulgides. The thermal stability of the *Z*-form fluorinated adamantylidene fulgides was predicted based upon the known decomposition pathway of the *Z*-form trifluoromethyl-substituted isopropylidene fulgide. Mechanistic studies have allowed for the rational design of more thermally stable *Z*-form fulgides.

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