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Thermolysis of fluorinated cycloalkylidene fulgides yields a new class of photochromic compounds†

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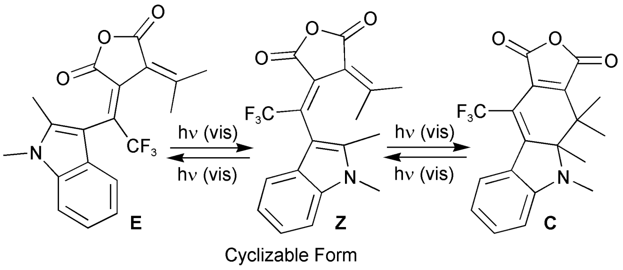
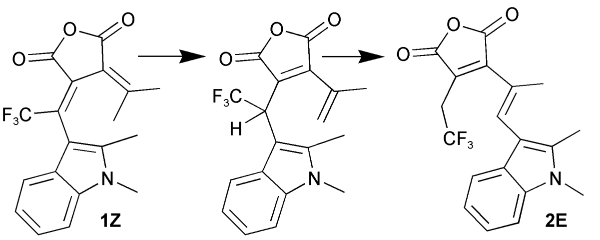
A series of fluorinated cycloalkylidene indolylfulgides has been designed, synthesized and characterized; most of the thermolysis products of these fulgides maintain photochromicity and display outstanding thermal and photochemical stability.

Photoactive organic compounds such as fulgides and diarylethenes have generated great interest as the photoactive media in high-density rewriteable optical memory devices.[1] The photoreversible nature of these compounds allows for repeated conversion between two key isomers with readily distinguishable absorption spectra.[2,3] Although numerous compounds have been prepared, few photochromic materials maintain the desired combination of photochemical and thermal stability essential for optical memory media. Recently discovered fluorinated indolylfulgides and their derivatives have demonstrated greatly enhanced resistance to photochemical fatigue relative to nonfluorinated analogues (Scheme 1).[4,5] Unfortunately, the trifluoromethyl group has been shown to destabilize the bridging alkene of the Z-form, resulting in loss of absorbance when subjected to elevated temperatures.[6] Herein, we describe the characterization of new thermally and photochemically stable photochromic materials derived from the thermal degradation of fluorinated indolylfulgides.



Scheme 1 Photoreactions of indolylfulgides. For fluorinated indolylfulgides, the cyclizable form is the Z-form (IUPAC nomenclature). For virtually all other fulgides the E and Z labels are reversed.

As previously reported, thermolysis of trifluoromethyl-substituted indolylfulgide **1Z** in refluxing toluene results in the formation of rearranged product **2E** (Scheme 2).[6] Noting that a central hexatriene unit is preserved in compound **2E**, we irradiated the molecule with 436 nm light and found evidence of E/Z and Z/C isomerization via thin layer chromatography. Based upon this indication of photochromic behavior, we then sought to design new photochromic compounds through the controlled thermal degradation of fluorinated indolylfulgides. The new materials, indolylethenylanhydrides, would be expected to maintain greater thermal stability than the parent fulgides while absorbing well into the visible region (**2E** was found to have an absorption maxima of 475 nm). To ensure that the hexatriene unit of the newly designed chromophore existed in the proper conformation for photochemical ring closure, the isopropylidene unit of **1Z** was replaced with a cycloalkylidene unit.[7] The resulting cycloalkylidene indolylfulgides would then be thermally degraded to yield the desired indolylethenylanhydrides.



Scheme 2 Thermolysis of indolylfulgide **1Z** at 110 °C in toluene.

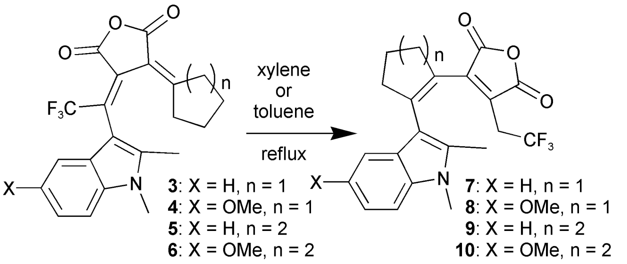
Fulgides **3–6** were synthesized using standard methods and displayed similar spectral characteristics in toluene to the previously studied fluorinated isopropylidene fulgides (Table 1, Scheme 3).[5,8–10] As hypothesized, cyclopentylidene fulgides **3** and **4** rearranged to the respective products **7** and **8** after 3 d in refluxing toluene (> 70% yield, Scheme 3). Rearrangement of the cyclohexylidene fulgides required more vigorous conditions. Indolylethenylanhydrides **9** and **10** were generated in approximately 30% yield after 5 d in refluxing *o*-xylene.

Each of the thermally rearranged indolylethenylanhydrides displayed considerable bathochromic shifts in the Z-form relative to their parent fulgides (Table 2). Methoxy-substituted cyclopentenyl derivative **8** displayed the longest wavelength maxima at nearly 500 nm. For compounds **8–10**, an accompanying blue shift of the C-form results in an overlap of the spectral features of the two forms (Fig. 1). The greatest spectral separation (~ 71 nm) between wavelength absorption maxima

Table 1 Quantum yields and extinction coefficients at λ_{max} for fulgides **3–6** in toluene

	λ_{max}/nm (ε_{max}/(mol^{-1} L cm^{-1}))			427 nm		559 nm	PSS^{427nm}
	Z-form	E-form	C-form	Φ_{ZC}	Φ_{CZ}	Φ_{CZ}	C:Z:E[a]
1[b]	427 (5300)	441 (5600)	571 (6400)	0.20	0.10	0.043	95:3:2
3	431 (5600)	444 (5400)	570 (5500)	0.17	0.052	0.032	88:3:9
4	438 (5100)	457 (6600)	615 (5200)	0.14	0.131	0.012	90:9:1
5	428 (4500)	443 (6600)	572 (5100)	0.08	0.055	0.087	91:7:2
6	433 (4700)	451 (7200)	617 (5200)	0.06	0.075	0.036	76:15:9

[a] Photostationary State (PSS). [b] Reference 5.



Scheme 3 Synthesis of indolylethenylanhydrides.

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† Electronic supplementary information (ESI) available: Synthetic procedures for **3–10**. Optical and stability characterization methods. See http://www.rsc.org/suppdata/cc/b3/b300010a/

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Table 2 Quantum yields and extinction coefficients at λ_{max} for indolylethenylanhydrides **7–10** in toluene

	λ_{max}/nm (ε_{max}/(mol^{-1} L cm^{-1}))		488 nm		605 nm	PSS^{488nm}
	Z-form	C-form	Φ_{ZC}	Φ_{CZ}	Φ_{CZ}	C:Z
7	485 (2000)	—[a]	—	—	—	—
8	495 (2400)	545 (5800)	0.016	0.044	0.044	20:80
9	460 (1200)	516 (6300)	0.071	0.043	0.037	28:72
10	464 (1100)	535 (6300)	0.063	0.028	0.018	38:62

[a] No C-form was obtained upon irradiation with visible light.

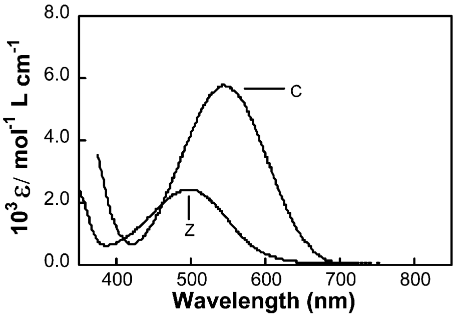
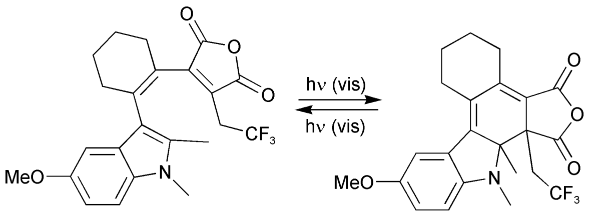


Fig. 1 Absorption spectra of indolylethenylanhydride **8** in toluene.

for the Z- and C-forms is evident for cyclohexenyl methoxy-substituted derivative **10**.

As suggested by our initial results with **2**, the Z-forms of indolylethenylanhydrides **8–10** were found to undergo photochemical electrocyclic ring closure, generating C-forms (Scheme 4). Photostationary states (PSS) containing appreciable amounts of both the C- and Z-forms of compounds **8–10** were obtained upon irradiation with 488 nm light (Fig. 2). In addition, each of the C-form compounds underwent quantitative cycloreversion to Z-form upon irradiation with > 630 nm light. Ring-closing quantum yields were greater for cyclohexenyl compounds **9** and **10**, while cyclopentenyl compound **8** displayed the highest ring-opening quantum yield when irradiated with 605 nm light.



Scheme 4 Photochemical reactions of methoxy-substituted indolylethenylanhydride **10**.

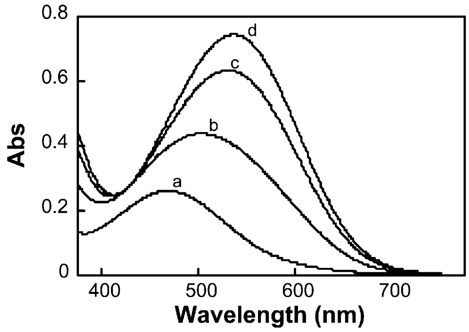


Fig. 2 Changing absorbance of a solution of methoxy-substituted indolylethenylanhydride **10Z** upon irradiation with 488 nm light; (a) 0 min, (b) 1 min, (c) 3 min, (d) 7 min.

Table 3 Thermal and photochemical stability of compounds **3–10**

	Thermal stability		Photochemical stability		
	A/A$_0$ (Z-form)[a]	A/A$_0$ (C-form)[a]	# of Cycles	A/A$_0$	%/ Cycle
3	0.29[b]	0.86	1200	0.81	0.018
4	0.28[b]	0.92	700	0.79	0.030
5	0.27[b]	0.49	900	0.81	0.023
6	0.27[b]	0.13	900	0.94	0.006
7	1.00[d]	–[c]	–[c]	–[c]	–[c]
8	1.00[d]	0.98	600	1.00[d]	0.00
9	1.00[d]	0.96	500	1.00[d]	0.00
10	1.00[d]	0.94	600	1.00[d]	0.00

[a] Absorbance at λ_{max} relative to initial absorbance after 168 h at 80 °C. [b] Residual absorbance due to thermolysis products. [c] No C-form generated. [d] No loss of absorbance within experimental error

The most notable characteristic of indolylethenylanhydrides was their outstanding thermal and photochemical stability (Table 3). While the Z-forms of cycloalkylidene fulgides **3–6** were fully decomposed within 4 h at 80 °C in PMMA, (poly(methyl methacrylate)), the corresponding indolylethenylanhydrides lost no absorbance after 3 weeks at 80 °C. The C-forms of **8–10** maintain comparable thermal stability. In addition, compounds **8–10** exhibited no loss of absorbance after 500 or more photochemical cycles in toluene (irradiation to 90% PSS with 436 nm light followed by quantitative bleaching with > 630 nm light). In comparison, bis(indolyl) diarylethenes degrade by more than 20% after 100 cycles in cyclohexane and are thermally unstable at room temperature.[11] Monoindolylmonothiophene diarylethenes are more thermally stable, > 12 h at 80 °C.[1] The thermal and photochemical stabilities of cycloalkylidene fulgides **3–6** were similar to previously studied fluorinated indolylfulgides.[5]

In summary, we have designed and synthesized a new class of photochromic compounds based upon the thermolysis of the fluorinated indolylfulgide precursors. The resulting indolylethenylanhydrides possess outstanding thermal and photochemical stability, making them candidates for a wide range of practical applications. Optimization of the spectral characteristics and examination of the wavelength dependency of the PSS compositions is ongoing.

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