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Synthesis and photochemistry of photochromic fluorescing indol-2-ylfulgimides

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A series of N-substituted, thermally stable, photochromic fluorescing indol-2-ylfulgimides were synthesized, with high yields, from the corresponding fulgides by Lewis acid and hexamethyldisilazane promoted one-pot reaction. The quantum efficiencies of the photoinduced coloration and bleaching processes, in polar and nonpolar solvents, were determined. The fluorescence quantum yields of the colored form as well as the thermal stability and fatigue resistances of the synthesized fulgimides were also determined.

1. Introduction

Photochromic materials have received increasing attention because of their potential application to rewritable high capacity optical memories, optical molecular switches, and high intensity light limiters.[1–3] Fulgides† belong to one of the most important families of photochromic molecules, because they show excellent photochromic behavior, and both forms are thermally stable and photoreversible. These properties make them potential materials for many electronic applications.[4,5] Even though a large number of useful molecules have been successfully synthesized, yet the search for new synthetic methods to tailor and make new photochromic molecules with the desired physical and chemical properties continues to be a challenging endeavor.

Fulgimides,‡ which are derivatives of fulgides, not only exhibit the excellent photochromic properties of their precursor fulgides, but in contrast to fulgides they are also chemically stable to acid or base-catalyzed hydrolysis.[6] An additional very attractive aspect of these fulgimides is that the introduction of various substituents at the nitrogen atom position of the imide ring can be used as a linking group to prepare photochromic copolymers, photochromic liquid crystals, photoregulated binding of proteins, and photochromic Langmuir–Blodgett films.[6–9]

In this paper, we describe a simple and efficient method, which we have used for the synthesis of photochromic indol-2-ylfulgimides. We also discuss the photochromic properties, including UV–visible absorption spectra, reaction efficiency of photoinduced ring-closing and ring-opening, fluorescence quantum efficiency, and fatigue resistance to the photochromic cycles of the synthesized fulgimides which we have studied.

2. Results and discussion

2.1. Synthesis of substituted fulgimides

The fulgimides reported so far have been synthesized, to a large extent, by the condensation of fulgides and amines followed by the cyclization of the N-substituted succinamic acid in the presence of acidic reagents, such as acetic anhydride, or acetyl chloride.[6,10] However, for this synthetic method, low reaction yields have been reported for the conversion of succinamic acids derived from fulgides with acid sensitive heterocyclic aromatic groups. Because of these low yields, the utilization of fulgimides in practical devices is bound to be limited.[11]

In this paper, we describe a method for the synthesis of fulgimides which is based upon the method described by Toru for the synthesis of *N*-alkyl and *N*-arylimide derivatives by Lewis acid and hexamethyldisilazane (HMDS) promoted one pot reaction.[12] Our data show that this is a simple and highly efficient method for the synthesis of heterocyclic aromatic ring substituted fulgimides. We used zinc chloride as Lewis acid; however no difference was found when we used zinc bromide instead of zinc chloride for the synthesis of **7g**.

The intermediates and fulgides were synthesized by the modified methods,[13–17] shown in Scheme 1.

2.2. UV–Vis absorption spectra of *E* and *C* Forms

The photochromic properties of the fulgimides, which we synthesized, were found to be similar to those of the precursor photochromic fulgides. When the open-ring *E* form (light yellow or colorless) of the fulgimide was irradiated with UV light, like fulgide, a conrotatory ring-closure reaction is assumed to occur, in agreement with the Woodward–Hoffmann selection rules (see Scheme 2).[18,19] This results in the formation of a cyclized structure (closed-ring form or *C* form) whose absorption spectrum is red shifted from ultraviolet to the visible region.

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Table 1 lists the absorption maxima and absorption coefficients of the fulgimides **7a**–**g**, *E* and *C* forms, in various solvents. The intensity maxima of the absorption spectra of the *E* forms are located between 370 and 390 nm, and to a large extent, they are not affected by solvent polarity. Substituents at the nitrogen atom of the imide ring did not have any influence on the absorption spectra maxima of the *E* form. Irradiation of the *E* form, with UV light, leads to the formation of the colored, *C* form, with absorption maxima in the 485–550 nm range. The position of the band maximum of the *C* form depends on the fulgimide structure and, in contrast to the *E*

†The IUPAC name for fulgides is 2,3-dialkylidenesuccinic anhydrides.
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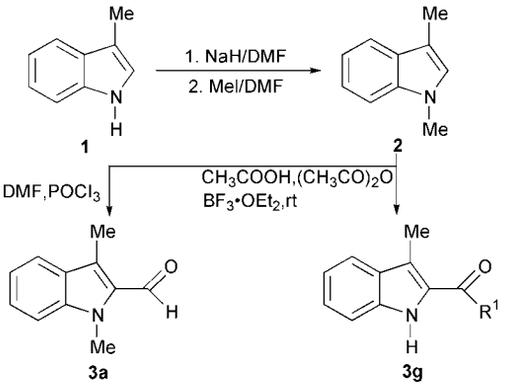
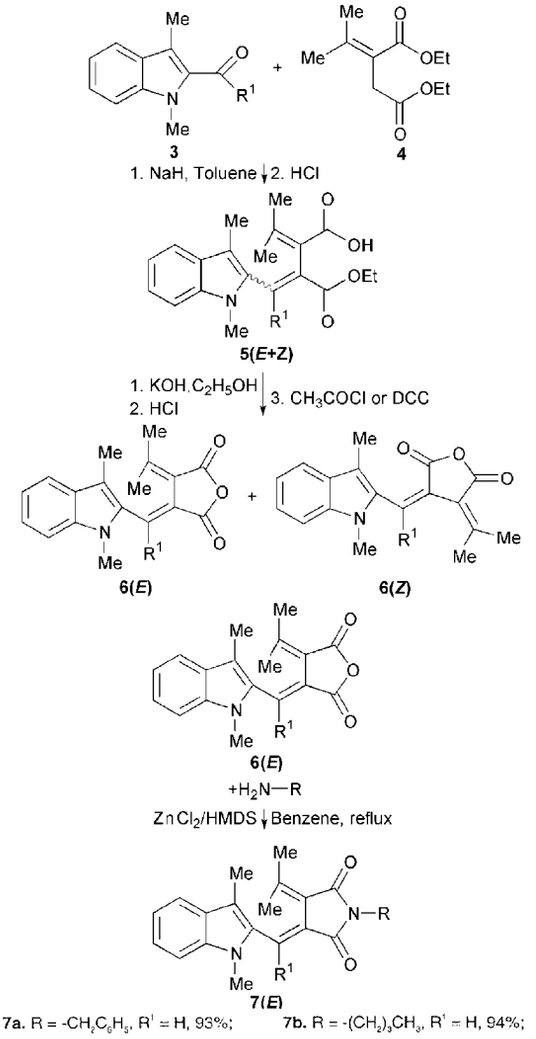
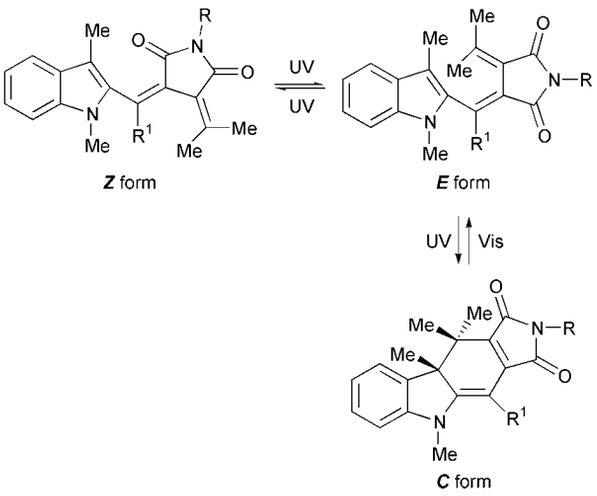


form, it also depends on solvent polarity. The shift to longer wavelengths, with increasing solvent polarity, and high absorption coefficients (larger than 10^4), support the assignment of the long wavelength absorption band of the colored form to a π–π^* transition.

The absorption maximum of the closed-ring, *C* form, is located in the 485–550 nm region, which is red shifted by about 145 nm compared to the corresponding open-ring, *E* form, in acetonitrile solution. The substituents at the N-position of the imide ring do not affect the absorption spectra maxima strongly. Comparison of nonpolar hexane with polar acetonitrile solutions reveals that the absorption maxima of the colored fulgimide forms are red shifted by 33 nm. This shift is smaller than the one observed for the corresponding colored fulgide, which is shifted by 40 nm under the same conditions. Polar solvents affect the absorption maximum of the *C* form, however they do not influence fulgides as much. This suggests that in the excited state, there is a large dipole moment formed which is stabilized by the polar solvent, but its magnitude is not as large as that observed for fulgides.



Scheme 1



Scheme 2

2.3. Photoreaction quantum yield

All of the fulgimides synthesized exhibit excellent photochromic properties. When **7a**–**7g** *E* forms are illuminated with UV light, they undergo photoinduced electrocyclic reaction, which generates the closed-ring structure *C* (see Scheme 2). The initially light yellow solutions of the **7a**–**g** open-ring form became red after excitation with 390 nm light. Fig. 1 shows the absorption spectra changes of **7g**, induced by 390 nm light. In parallel with the ring-closing process, photoisomerization between the *E* and *Z* forms also takes place, which is evident in the proton NMR spectrum and the shift of the isosbestic point (see Fig. 1). Because there is more than a 140 nm Stokes shift between the absorption spectra of the *E* and *C* forms, where the *C* form has a much smaller absorption at 390 nm, we were able to convert the open-ring *E* form, almost quantitatively, to the *C* form by excitation of the *E* form with 390 nm light. All experiments were performed in acetonitrile. It should be noted however that the absorption spectra of the *E* and *Z* forms vary only slightly, therefore photoexcitation with 390 nm light, where both forms have strong absorption, leads to the formation of a photoequilibrium mixture between these two forms at the initial stage of irradiation. Because there is no photoequilibrium between *C* and *E* or *C* and *Z*, the generated *Z* isomer would finally go to the *C* form through the *E* isomer. The colored form can be reversed back to the open-ring, bleached form, by excitation with light at $\lambda > 530$ nm. During the ring-opening process the formation of only the *E* form was observed (see Fig. 2), which is the favorite configuration for the cyclization process.

The quantum yields of ring-closing (coloration) and ring-opening (bleaching) of indol-2-ylfulgimides were measured in the solvents listed in Table 2. The data show that, in polar solvents such as acetonitrile, the quantum yield of **7a**–**7f** *E* to *C* conversion is about 0.14. However, **7g** has a quantum yield of 0.33; this variation in the quantum yield appears because they are derived from different precursor fulgides which have quantum yields varying from 0.12 to 0.26 depending on their structures. In nonpolar solvents, such as hexane, the quantum yields are about the same as in polar solvents. The quantum

Table 1 UV–Vis maximum absorption and absorption coefficients of *E* and *C* forms of indol-2-ylfulgimides in various solvents

Samples CH_3CN	Isomer	λ_{max}/nm (ε/L mol^{-1} cm^{-1})			
		$C_2H_4Cl_2$	$CH_3C_6H_5$	Hexane	
7a	*E*	374 (1.37×10^4)	383 (1.41×10^4)	384 (1.35×10^4)	381 (1.38×10^4)
	C	522 (1.05×10^4)	520 (1.06×10^4)	508 (1.02×10^4)	487 (1.02×10^4)
7b	*E*	371 (1.36×10^4)	378 (1.38×10^4)	383 (1.37×10^4)	378 (1.39×10^4)
	C	517 (1.02×10^4)	517 (1.02×10^4)	505 (1.01×10^4)	484 (1.01×10^4)
7c	*E*	373 (1.33×10^4)	380 (1.40×10^4)	384 (1.35×10^4)	379 (1.39×10^4)
	C	519 (1.04×10^4)	519 (1.05×10^4)	506 (1.02×10^4)	485 (1.04×10^4)
7d	*E*	382 (1.52×10^4)	390 (1.55×10^4)	393 (1.53×10^4)	390 (1.59×10^4)
	C	526 (1.08×10^4)	526 (1.08×10^4)	514 (1.01×10^4)	494 (1.01×10^4)
7e	*E*	380 (1.47×10^4)	388 (1.51×10^4)	390 (1.47×10^4)	387 (1.52×10^4)
	C	523 (1.11×10^4)	524 (1.11×10^4)	512 (1.05×10^4)	492 (1.07×10^4)
7f	*E*	386 (1.35×10^4)	394 (1.40×10^4)	398 (1.36×10^4)	393 (1.41×10^4)
	C	529 (1.03×10^4)	529 (1.04×10^4)	517 (1.00×10^4)	496 (1.00×10^4)
7g	*E*	360 (7.63×10^3)	369 (7.99×10^3)	372 (7.74×10^3)	369 (8.13×10^3)
	C	553 (8.91×10^3)	552 (9.14×10^3)	537 (9.72×10^3)	516 (8.80×10^3)

yields of the ring-opening processes of fulgimides are found to be 0.08 in acetonitrile, and are related to the substituent groups at the nitrogen atom of the imide ring. The quantum yield of the ring-opening process of fulgimides *C* to *E* depends on the polarity of the solvents. In nonpolar hexane, the quantum yield of the ring-opening processes is about two times larger than in acetonitrile, which places them near the values of the corresponding fulgides.[5] These data are presented in Table 2. The fact that low quantum yields were observed in polar solvents may be explained by the strong interaction between the polar excited state of the fulgimide *C* form and the polar solvent, which may raise the activation energy of the ring-opening process and consequently decrease the transformation rate. Using different substituting groups at the nitrogen atom position of the imide ring, we found that the effect on the quantum yield of the coloration process is not significant.

2.4. Thermal stability and fatigue resistance

It is very important for technological applications that the media are thermally stable, in both forms. In other words, the photochromic isomers can not be thermally interconverted at room temperature. Thermal stability is therefore a mandatory property of the long-term information storage media and electronic switching devices. We have measured the thermal stability of the *E* and *C* forms of our fulgimides, and the data show that all the isomeric forms of fulgimides **7a**–**7g** have excellent long term, room temperature, thermal stability. No changes owing to temperature were detected by means of NMR and UV–Vis absorption spectroscopy, when pure *E* and *C* forms were dissolved in chloroform-d_3 or acetonitrile solvents and kept in the dark at room temperature for over one month. This suggests, strongly, that no thermal transformation between different isomers occurred at room temperature during the time of this test period.

We have also investigated the fatigue resistance of our fulgimide as a function of ring-closing/ring-opening cycles. Here the fatigue resistance is defined as, after a certain number of ring-closing/ring-opening (or coloration/bleaching) cycles, the percentage of the molecules still retaining the photochromic properties.

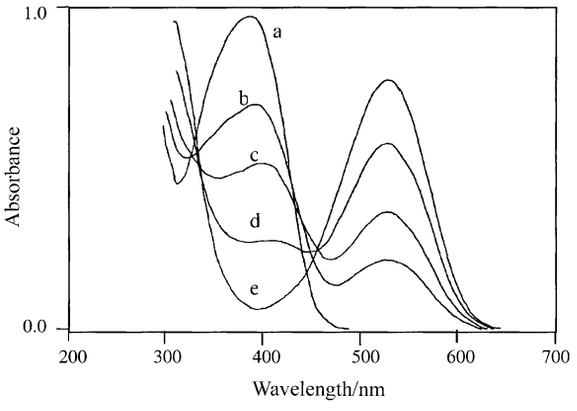


Fig. 1 Absorbance change, ΔA, *vs.* λ of **7f**, *E* form, in acetonitrile, irradiated with 390 nm light; a, before irradiation; b, c, d, and e, after 1 minute, 2.3 minutes, 8 minutes, and 30 minutes respectively.

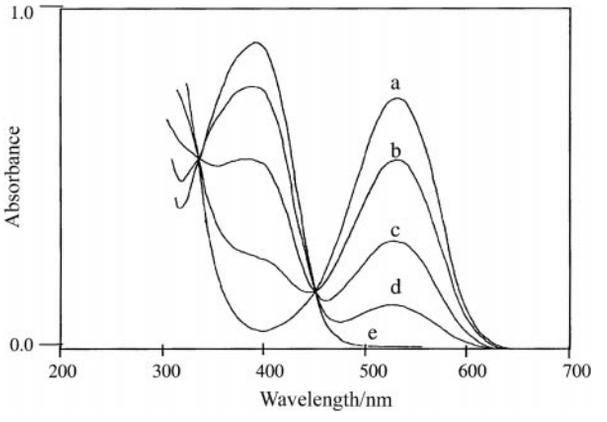


Fig. 2 Change in optical density, ΔA, *vs.* λ, for **7f** *C* form in acetonitrile irradiated with 530 nm light; a, initial colored form; b, c, d, and e, after 1.3 minute, 4 minutes, 8 minutes, and 16 minutes respectively.

Table 2 Quantum yield of photocoloration and photobleaching of indol-2-ylfulgimides in several solvents

	Φ_{E-C} ($\lambda_{ex}=350$ nm)		Φ_{C-E} ($\lambda_{ex}=500$ nm)	
Samples	CH_3CN	Hexane	CH_3CN	Hexane
7a	0.13	0.14	0.076	0.30
7b	0.14	0.15	0.11	0.30
7c	0.14	0.15	0.11	0.30
7d	0.14	0.15	0.068	0.25
7e	0.13	0.14	0.083	0.28
7f	0.15	0.15	0.048	0.23
7g	0.33	0.29	0.062	0.20

A ring-closing/ring-opening cycle refers to the transformation of more than 80% of the *E* form to *C* form and the subsequent complete conversion back to the *E* form. In Fig. 3, we display the ratio of the *C* form of the non-decomposed fulgimide acetonitrile solution to the original form after a number of photochromic ring-closing/ring-opening cycles. Our result shows that indol-2-ylfulgimide, like its precursor, exhibits excellent fatigue resistance. We have tried but failed to figure out the structure of the decomposition products generated during the photochromic cycles, because multi-pathway decomposition reactions were involved, which were evidenced by the TLC plate. The experimental data also show that substitution at the nitrogen atom position of the imide ring does not affect the fatigue resistance.

2.5. Fluorescence quantum yield

In contrast to the previously investigated fulgimides which do not emit fluorescence,[11] the closed-ring forms *C* of fulgimides **7a**–**7f**, which we synthesized, emit fluorescence (see Fig. 4c). The fluorescence spectrum of the *C* forms in acetonitrile shows a broad emission band with its intensity maximum around 650 nm. To confirm that the observed fluorescence is emitted by the closed-ring form of these fulgimides, rather than from impurities or other species, we measured the excitation spectra and fluorescence emission intensity changes as a function of ring-opening/ring-closing cycles. The data show that the intensity of fluorescence and excitation spectra of the closed-ring form decrease proportionally with the concentration of the fulgimide closed-ring form (see Fig. 5). When the solution was completely bleached, *i.e.* the absorption band of the *C* form completely disappeared, no fluorescence was detected. When the bleached solutions were colored again by excitation with

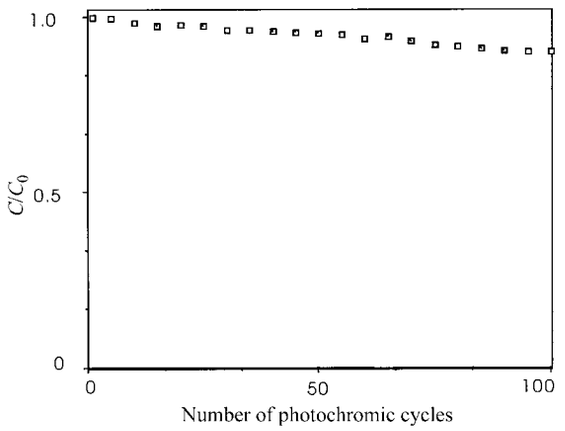


Fig. 3 Fatigue, defined as ratio of fulgimide **7b** colored form to original, in acetonitrile, as a function of number of coloration/bleaching cycles.

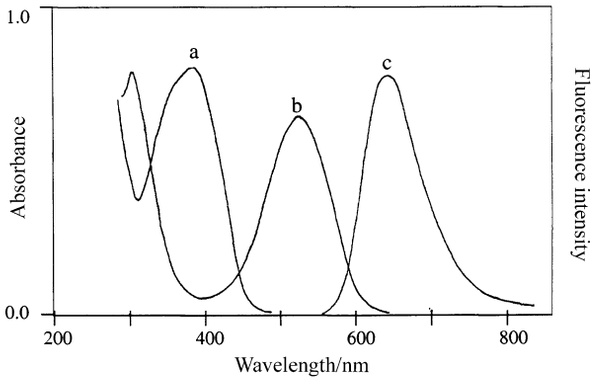


Fig. 4 Absorption and fluorescence spectra of fulgimide **7f** in acetonitrile: a, absorption spectrum of *E* form; b and c, absorption and fluorescence spectra of *C* form.

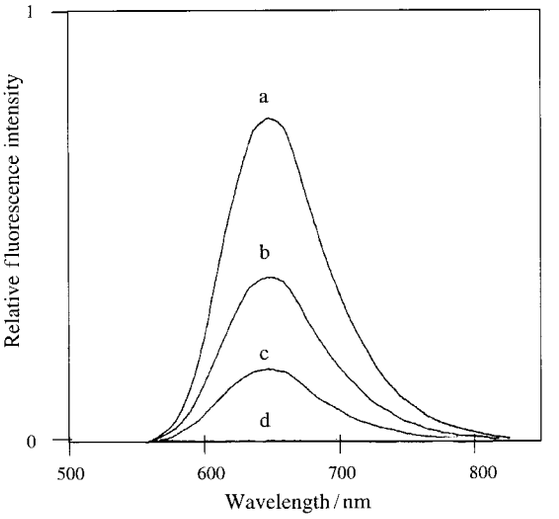


Fig. 5 Fluorescence intensity *vs.* λ for **7f**, *C* form, in acetonitrile, excited with 530 nm light; a, initial colored form; b, c, and d: after 1 minute, 2.5 minutes and 8 minutes irradiation respectively.

390 nm light, the fluorescence appeared again and increased at the same rate as the growth rate of the *C* form.

These data strongly support our proposal that the observed fluorescence is emitted only by the *C* form of the fulgimides, rather than any impurities or decomposition products. In Table 3 we list the fluorescence quantum yields of the colored fulgimides in acetonitrile solution. The experimental data indicate that the quantum yield of the fluorescence does not depend strongly on substituents at the nitrogen atom of the imide ring. No fluorescence was detected from the *E* forms of the fulgimides **7a**–**7g**.

3. Conclusion

We have successfully synthesized, with high yield, a series of novel photochromic fluorescent indol-2-ylfulgimides, by means of a simple and efficient Lewis acid and hexamethyldisilazane promoted one-pot reaction. This method may be also suitable for the transformation of a wide range of other heterocyclic fulgides to the corresponding fulgimides. We have also determined the photochromic properties, such as UV–visible absorption, coloration, bleaching and fluorescence quantum efficiency, and photochromic cycle fatigue resistance of these fulgimides. The data show that these newly synthesized fulgimides have very similar photochromic properties to those of the original fulgides.

Table 3 Relative fluorescence quantum yields of colored indol-2-ylfulgides in various solvents

Samples	Φ ($\lambda_{ex}=514$ nm) CH_3CN	Φ ($\lambda_{ex}=550$ nm) CH_3CN
7a	0.018	0.033
7b	0.014	0.025
7c	0.017	0.031
7d	0.041	0.073
7e	0.040	0.068
7f	0.046	0.073
7g	—	7.3×10^{-4}

4. Experimental section

4.1. General experimental details

Fulgimides **7a**–**7g** (Scheme 1) *E* forms were obtained directly by Lewis acid and hexamethyldisilazane (HMDS) promoted one-pot reaction followed by column chromatography purification and subsequently recrystallization. The closed-ring forms (*C* form) of these fulgimides were prepared by irradiating the *E* form of the fulgimides in an acetonitrile solution with 390 nm light, and the subsequent removal of the solvent under reduced pressure. The structure and purity of the compounds obtained were ascertained by NMR, MS and elemental analysis. All the solvents were HPLC grade or spectroscopic grade and were used without further purification. All spectra and quantum yields were measured in 1 cm quartz cells at room temperature. The UV–Vis absorption and fluorescence spectra were recorded with a Shimadzu UV 160 spectrophotometer and a Shimadzu RF 5000U spectrofluorophotometer, respectively.

Photoirradiation was carried out with a 150 W Xenon arc lamp (Oriel). The appropriate wavelength was selected by either a monochromator, placed between the lamp and the sample, or a cut off optical filter. The methods which we used to determine the quantum efficiency of the photochromic reaction, *i.e.* ring-closing (coloration) and ring-opening (bleaching), and the fluorescence quantum yields were the same as those described in our previous publication.[5]

4.2. Synthesis of materials

The synthesis of fulgimides was performed as follows: into a solution of fulgide **6**[5] (0.233 g, 0.79 mmol) in benzene (12 mL), benzylamine (0.79 mmol) in benzene (5 mL) was added and stirred for one hour at room temperature. To this reaction mixture, zinc chloride powder (0.79 mmol) was added in one portion. Subsequently, the reaction mixture was heated to refluxing temperature (80 °C), and a solution of hexamethyldisilazane (HMDS) (0.26 ml, 1.2 mmol) in benzene (5 ml) was added within 10 min. This reaction mixture was then refluxed for 4 hours. The reaction process was monitored by TLC. After removal of the solvent with a rotavapor, the crude product was purified by means of flash silica gel column chromatography (chloroform as eluent) to afford a bright yellow solid **7a** (0.284 g, 93%). Fulgimides **7b**–**7g** were synthesized by similar methods but with different reaction times.

***N*-Benzyl-2-[1,3-dimethylindol-2-ylmethylidene]-3-isopropylidenesuccinimide (7a).** Mp:178.5–179.5 °C, ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.25 (s, 3H), 1.94 (s, 3H), 2.47 (s, 3H), 3.70 (s, 3H), 4.81–4.85 (m, 2H), 7.10–7.65 (m, 10H); ^{13}C NMR (500 MHz, $CDCl_3$, TMS) δ 10.6, 22.6, 26.9, 30.8, 41.8, 109.1, 115.1, 119.5, 121.2, 122.4, 123.5, 127.1, 127.6, 127.7, 128.4, 128.6, 132.8, 136.5, 138.4, 153.5, 168.3, 168.9; HRMS (CI) *m*/*z* calcd for $C_{25}H_{24}N_2O_2$ 384.1838 (M^+), found 384.1833; Anal. Calcd for $C_{25}H_{24}N_2O_2$: C, 78.09; H, 6.30; N, 7.29. Found: C, 77.37; H, 6.26; N, 7.18%.

***N*-Butyl-2-[1,3-dimethylindol-2-ylmethylidene]-3-isopropylidenesuccinimide (7b).** Mp: 153.5–154.5 °C, ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 0.97 (t, $J=7.3$ Hz, 3H), 1.26 (s, 3H), 1.38 (sextet, $J=7.3$ Hz, 2H), 1.63–1.69 (m, 2H), 1.95 (s, 3H), 2.48 (s, 3H), 3.67 (td, $J=7.2$, 4.2 Hz, 2H), 3.72 (s, 3H), 7.13–7.62 (m, 5H); ^{13}C NMR (500 MHz, $CDCl_3$, TMS) δ 10.5, 13.7, 20.2, 22.4, 26.8, 30.2, 30.7, 38.0, 109.0, 114.8, 119.4, 120.7, 122.3, 123.4, 127.3, 127.5, 132.8, 138.3, 152.8, 168.7, 169.2; HRMS (CI): Calcd for $C_{22}H_{26}N_2O_2$: *m*/*z* 350.1994 (M^+); Found: 350.1977; Anal. Calcd for $C_{22}H_{26}N_2O_2$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.33; H, 7.44; N, 7.97%.

***N*-Allyl-2-[1,3-dimethylindol-2-ylmethylidene]-3-isopropylidenesuccinimide (7c).** Mp: 131.5–133.0 °C, ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.27 (s, 3H), 1.96 (s, 3H), 2.48 (s, 3H), 3.73 (s, 3H), 4.10–4.31 (m, 2H), 5.22 (d, $J=10.2$ Hz, H), 5.29 (d, $J=17.1$ Hz, H), 5.87–5.94 (m, H), 7.13–7.65 (m, 5H); ^{13}C NMR (500 MHz, $CDCl_3$, TMS) δ 10.6, 22.5, 26.9, 30.8, 40.3, 109.1, 115.0, 117.7, 119.5, 121.1, 122.3, 123.5, 127.2, 127.6, 131.4, 132.8, 138.4, 153.4, 168.2, 168.8; HRMS (CI): Calcd for $C_{21}H_{22}N_2O_2$: *m*/*z* 334.1681 (M^+); Found: 334.1674; Anal. Calcd for $C_{21}H_{22}N_2O_2$: C, 75.42; H, 6.63; N, 8.38. Found: C, 75.25; H, 6.63; N, 8.30%.

2-[1,3-Dimethylindol-2-ylmethylidene]-3-isopropylidene-*N*-(4-vinylphenyl)succinimide (7d). Mp: 192.5–194.5 °C, ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.33 (s, 3H), 2.01 (s, 3H), 2.52 (s, 3H), 3.75 (s, 3H), 5.30 (d, $J=10.9$ Hz, H), 5.78 (d, $J=17.6$ Hz, H), 6.73 (dd, $J=17.6$, 10.9 Hz, H), 7.16–7.76 (m, 9H); ^{13}C NMR (300 MHz, $CDCl_3$, TMS) δ 10.8, 22.7, 27.1, 30.8, 109.1, 114.9, 115.4, 119.5, 119.6, 121.8, 123.6, 126.6, 126.7, 132.8, 136.0, 137.5, 138.5, 154.3, 167.5, 168.2; HRMS (CI): Calcd for $C_{26}H_{24}N_2O_2$: *m*/*z* 396.1838 (M^+); Found: 396.1826; Anal. Calcd for $C_{26}H_{24}N_2O_2$: C, 78.76; H, 6.10; N, 7.07. Found: C, 78.55; H, 6.13; N, 7.05%.

2-[1,3-Dimethylindol-2-ylmethylidene]-3-isopropylidene-*N*-phenylsuccinimide (7e). Mp: 167.5–168.5 °C, ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.33 (s, 3H), 2.01 (s, 3H), 2.52 (s, 3H), 3.74 (s, 3H), 7.13–7.76 (m, 10H); ^{13}C NMR (300 MHz, $CDCl_3$, TMS) δ 10.7, 22.7, 27.0, 30.8, 109.0, 115.3, 119.4, 119.5, 121.7, 122.1, 123.6, 126.6, 126.7, 127.5, 128.1, 128.9, 131.9, 132.7, 138.4, 154.2, 167.5, 168.2; HRMS (CI): Calcd for $C_{24}H_{22}N_2O_2$: *m*/*z* 370.1681 (M^+); Found: 370.1676; Anal. Calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.23; H, 5.98; N, 7.52%.

2-[1,3-Dimethylindol-2-ylmethylidene]-3-isopropylidene-*N*-(4-ethoxycarbonylbenzyl)succinimide (7f). Mp: 159.5–160.5 °C, ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.34 (s, 3H), 1.41 (t, $J=7.1$ Hz, 3H), 2.01 (s, 3H), 2.53 (s, 3H), 3.77 (s, 3H), 4.40 (q, $J=7.1$ Hz, 2H), 7.10–8.19 (m, 9H); ^{13}C NMR (500 MHz, $CDCl_3$, TMS) δ 10.8, 14.3, 22.8, 27.2, 30.8, 61.12, 109.1, 115.6, 119.5, 119.6, 122.2, 123.8, 126.2, 126.3, 129.8, 130.2, 132.7, 136.0, 138.5, 154.9, 165.8, 167.0, 167.9; HRMS (CI): Calcd for $C_{27}H_{26}N_2O_4$: *m*/*z* 442.1892 (M^+); Found: 442.1877.

***N*-Benzyl-2-[1-(1,3-dimethylindol-2-yl)ethylidene]-3-isopropylidenesuccinimide (7g).** Mp: 60–61 °C, ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.00 (s, 3H), 2.04 (s, 3H), 2.24 (s, 3H), 2.65 (s, 3H), 3.62 (s, 3H), 4.78–4.84 (m, 2H), 7.11–7.45 (m, 9H); ^{13}C NMR (500 MHz, $CDCl_3$, TMS) δ 10.0, 22.1, 22.4, 25.3, 31.5, 41.3, 109.0, 109.7, 119.4, 122.7, 122.9, 127.6, 127.8, 128.5, 128.6, 136.6, 137.5, 138.1, 138.8, 150.8, 167.9, 168.2; HRMS (CI): Calcd for $C_{26}H_{26}N_2O_2$: *m*/*z* 398.1994 (M^+); Found: 398.1986; Anal. Calcd for $C_{26}H_{26}N_2O_2$: C, 78.50; H, 6.58; N, 7.03. Found: C, 78.28; H, 6.70; N, 6.90%.

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