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Articles

Thermochromic Fluorophores and Their NIR Laser Induced Transformation

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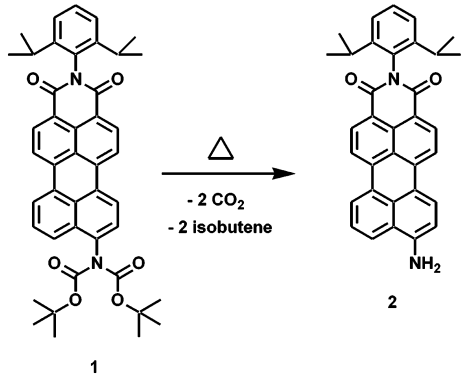
Novel thermochromic fluorophores with high fluorescence efficiencies have been prepared. When these fluorophores are treated with heat they undergo an irreversible change from a colorless low-fluorescent state to a colorless strongly fluorescent state. Beyond this, we demonstrate how the irreversible change of a thermochromic fluorophore can be induced via near-infrared (NIR) laser light and point out distinct advantages of this approach for high-density optical data storage.

1. Introduction

Materials that can be transformed between two clearly distinguishable states by an external stimulus find many technological applications as “smart materials”. In particular, thermochromic dyes are important for a number of applications such as laser marking[1] and optical data storage.[2] Such a property was demonstrated for the conversion of an alkoxycarbonylated amino-substituted perylenedicarboximide **1** (see Scheme 1). By thermal fragmentation of the alkoxycarbonylated amino group, another fluorophore, 9-aminoperylenedicarboximide **2**,[3] is obtained (see Scheme 1). Importantly, both the absorption and the fluorescence spectra of **1** and **2** are clearly different (Figure 1), allowing for an easy optical discrimination. Here, we are presenting two investigations aiming for a wider applicability of thermochromic fluorophores.

Scheme 1. Irreversible Thermal Fragmentation of the Thermochromic Perylene Dye 1



In the first part, we describe a synthetic route for the development of thermochromic fluorophores with different spectral properties that provide more flexibility in applications. Especially compounds with transitions in the UV could be advantageous for laser-marking applications,[4−10] as they provide marks invisible to the naked eye. Possible applications range from security to automatic identification purposes,[1] such as bar coding of articles, durable imprinting of returnable goods, or proper grading and recycling of plastics.[2] To achieve this goal, we applied our method of heat-induced transformation of an alkoxycarbonylated amino-substituted perylenedicarboximide **1** (Scheme 1). Novel thermochromic fluorophores with donor-substituted pthalimides with optical transitions in the UV range were synthesized and are presented in this paper.

In the second part of this paper, we demonstrate that with the aid of a NIR absorber the thermal fragmentation of thermochromic dyes can be induced by laser light. This is desirable from a technological point of view, because it allows a quick and easy processing that does not require contact with the material. This laser-induced transformation envisages a number of new applications for thermochromic dyes, e.g. laser marking and optical data storage.

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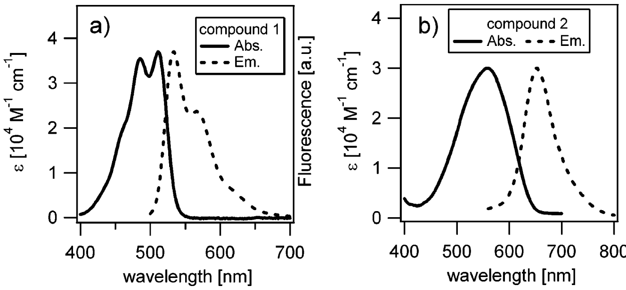

Figure 1. Absorption and fluorescence emission spectra ($CHCl_3$) of (A) compound **1** (emission spectrum recorded at $\lambda_{ex} = 480$ nm) and (B) compound **2** (emission spectrum recorded at $\lambda_{ex} = 550$ nm).

2. Experimental Section

General. The solvents used were of commercial grade. Perylenemonoimide was supplied by BASF AG. Column chromatography was performed on silica gel (Geduran Si60, Merck). Experimental ^{1}H and ^{13}C NMR were recorded on a Bruker Avanche 250, Bruker AMX 300, and Infrared spectra were obtained on a Nicolet FT IR 320. Fd mass spectra were performed with a VG-Instruments ZAB 2-SE-FDP instrument. UV/vis spectra were recorded on a Perkin-Elmer Lambda 9 and fluorescence spectra on a SPEX Fluorolog 3 spectrometer. The elemental analyses were performed by the Department of Chemistry and Pharmacy of the University of Mainz. Approximate fluorescence quantum yields were obtained for solutions of the compounds **3**, **4**, **7**, and **9** in chloroform using coumarin in ethanol with a known quantum yield of 0.64[11] as reference.

Laser-Marking Experiment. Compounds **1** and **2** were synthesized according to a procedure that was already reported.[3] The NIR absorber bis(perylenedicarboximide)-*a,d*-1,5-diaminoanthraquinone was obtained as described in ref 12. Compound **1** (7×10^{-3} M), a NIR absorber (4×10^{-3} M), and polystyrene (20 g/L; Polymer Standard Services, Mainz, Germany, $M_w = 65000$; $M_w/M_n = 1.02$) were dissolved in toluene (99.96 %, Fischer Scientific) and spin-coated on a BK7-glass slide, leading to a film with a thickness of 300 nm as checked by a surface profiler (Tencor P-10). The samples were mounted on a heating stage, and the temperature was measured with a Pt-100 thermocouple on the surface of the films and kept constant (to less than ±0.5 °C) with a closed-loop PID controller. The beam of an NIR laser (Nd:YAG, 1064 nm, 50 mW, Amoco Laser Co., 1064-EHA) was focused on the sample with a standard 5× microscope objective, yielding a spot with a diameter of approximately 100 μm. Absorption and fluorescence spectra were recorded with a Perkin-Elmer Lambda 900 UV−vis−NIR spectrometer and a Spex Fluorolog fluorescence spectrometer, respectively. Fluorescence micrographs were obtained with a conventional fluorescence microscope (Olympus IX50), equipped with a color CCD camera (Zeiss Axiocam). A Hg-vapor lamp served as the light source, and appropriate combinations of optical filters were used to select excitation wavelength λ_{ex} and emission wavelength λ_{em} ($\lambda_{ex} = 480$ nm, $\lambda_{em} > 515$ nm or, alternatively, $\lambda_{ex} = 540$ nm, $\lambda_{em} > 590$ nm).

***N*-(2,6-Diisopropylphenyl)-3-nitrobenzene-1,2-dicarboximide (6).** 3-Nitro-1,2-anhydride (5 g, 26 mmol) and 2,6-diisopropylaniline (13.8 g, 78 mmol) were stirred in 100 mL of propionic acid. The reaction mixture was refluxed for 16 h under argon. After cooling to room temperature, the crude product was precipitated with water, filtered, and resuspended in hydrochloric acid. The resulting precipitate was filtered again, washed with water, and dried under vacuum, affording 8.6 g (94% yield) of the title compound as a colorless solid: mp 178 °C; ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 300 K) $\delta = 8.15-8.12$ (m, 2 H), 7.92 (t, $^3J = 8.0$ Hz, 1 H), 7.41 (t, $^3J = 8.0$ Hz, 1 H), 7.22 (d, $^3J = 8.0$ Hz, 2 H), 2.55 (sept, $^3J = 6.9$ Hz, 2 H), 1.08 (d, $^3J = 6.9$ Hz, 6 H), 1.07 (d, $^3J = 6.9$ Hz, 6 H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 300 K) $\delta = 165.88$ (C═O), 162.93 (C═O), 147.27, 145.42, 136.21, 133.97, 130.80, 129.38, 128.22, 126.41, 124.39, 123.76, 29.69, 24.38, 24.28; IR (KBr) $\nu = 2967$, 2870, 2363, 1786, 1728, 1705, 1618, 1541, 1466, 1370, 1250, 1119, 1053, 876, 831, 767, 721 cm^{-1}; MS (FD 8 kV) *m/z* (rel int) = 352.0 (100%) [M$^+$]. Anal. Calcd for $C_{20}H_{20}N_2O_4$: C 68.17, H 5.72, N 7.95. Found: C 68.20, H 5.67, N 7.92.

***N*-(2,6-Diisopropylphenyl)-3-aminobenzene-1,2-dicarboximide (7).** A solution of 3 g (8.5 mmol) of *N*-(2,6-diisopropylphenyl)-3-nitrobenzene-1,2-dicarboximide in 150 mL of ethanol was reduced under hydrogen atmosphere in the presence of 200 mg of palladium on activated carbon (10%). After 16 h at room temperature, palladium on activated carbon was removed by filtration and the solvent of the remaining solution was evaporated. The crude product was purified by column chromatography on silica gel using CH_2Cl_2 as eluent, affording 2.4 g (89% yield) of a slightly yellow solid: mp 251 °C; ^{1}H NMR (250 MHz, $C_2D_2Cl_4$, 300 K) $\delta = 7.69$ (t, $^3J = 8.2$ Hz, 1 H, H), 7.36 (t, $^3J = 7.6$ Hz, 1 H), 7.19 (d, $^3J = 7.6$ Hz, 2 H), 7.16 (d, $^3J = 6.6$ Hz, 1 H), 6.86 (d, $^3J = 8.2$ Hz, 1 H), 5.23 (s, 2 H, NH_2), 2.64 (sept, $^3J = 6.6$ Hz, 2 H), 1.08 (d, $^3J = 6.6$ Hz, 6 H), 1.05 (d, $^3J = 6.6$ Hz, 6 H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 300 K) $\delta = 170.21$ (C═O), 168.57 (C═O), 147.66, 145.89, 135.85, 132.75, 130.15, 127.33, 124.11, 121.69, 113.52, 111.43, 29.48, 24.37; IR (KBr) $\nu = 3470$, 3354, 2965, 2871, 1744, 1706, 1692, 1633, 1592, 1483, 1463, 1403, 1366, 1336, 1248, 1196, 1138, 1110, 1094, 1055, 1024, 967, 877, 823, 799, 745 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (ϵ) = 392 nm (5700 M^{-1} cm^{-1}); fluorescence ($CHCl_3$, excitation 390 nm) $\lambda_{max} = 458$ nm; MS (FD 8 kV) *m/z* (rel int) = 322.3 (100) [M$^+$]. Anal. Calcd for $C_{20}H_{22}N_2O_2$: C 74.51, H 6.88, N 8.69. Found: C 74.53, H 6.75, N 8.71.

***N*-(2,6-Diisopropylphenyl)-3-hydroxybenzene-1,2-dicarboximide (9).** The synthesis was performed as described for **6**. Modifications included the following: 2.1 g (13 mmol) of 3-hydroxy-1,2-anhydride, 6.9 g (39 mmol) of 2,6-diisopropylaniline, and 50 mL of propionic acid. The desired product was obtained as a colorless solid (3.8 g, 92%): mp 157 °C; ^{1}H NMR (250 MHz, $C_2D_2Cl_4$, 300 K) $\delta = 7.65-7.59$ (m, 2 H), 7.44−7.35 (m, 2 H), 7.22 (s, 1 H, OH), 7.18 (d, $^3J = 7.5$ Hz, 2 H), 2.61 (sept, $^3J = 6.7$ Hz, 2 H), 1.09 (d, $^3J = 6.7$ Hz, 6 H), 1.06 (d, $^3J = 6.7$ Hz, 6 H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 300 K) $\delta = 170.52$ (C═O), 167.92 (C═O), 155.18, 147.56, 137.19, 131.96, 130.49, 126.56, 124.26, 123.31, 116.94, 114.73, 29.58, 24.39, 24.30; IR (KBr) $\nu = 3557$, 3470, 3432, 2966, 2870, 1774, 1710, 1695, 1614, 1463, 1392, 1369, 1300, 1281, 1252, 1218, 1164, 1113, 1101, 1058, 1032, 979, 880, 822, 801, 752, 696, 600, 561 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (ϵ) = 349 nm (5300 M^{-1} cm^{-1}); fluorescence ($CHCl_3$, excitation 345 nm) $\lambda_{max} = 524$ nm; MS (FD 8 kV) *m/z* (rel int) = 323.1 (100) [M$^+$]. Anal. Calcd for $C_{20}H_{21}NO_3$: C 74.28, H 6.55, N 4.33. Found: C 74.21, H 6.61, N 4.27.

N-(2,6-Diisopropylphenyl)-3-(di-*tert*-butoxycarbonylamino)-benzene-1,2-dicarboximide (3). *N*-(2,6-Diisopropylphenyl)-3-aminobenzene-1,2-dicarboximide **(**1 g, 3.1 mmol) was dissolved in 80 mL of dry THF. To this solution was added 2.7 g (12.4 mmol) of di-*tert*-butyl dicarbonate and 73 mg (0.6 mmol) of 4-*N*,*N*-dimethylaminopyridine. The reaction mixture was stirred for 12 h at room temperature before the solvent was evaporated. The crude product was purified by column chromatography on silica gel with CH_2Cl_2

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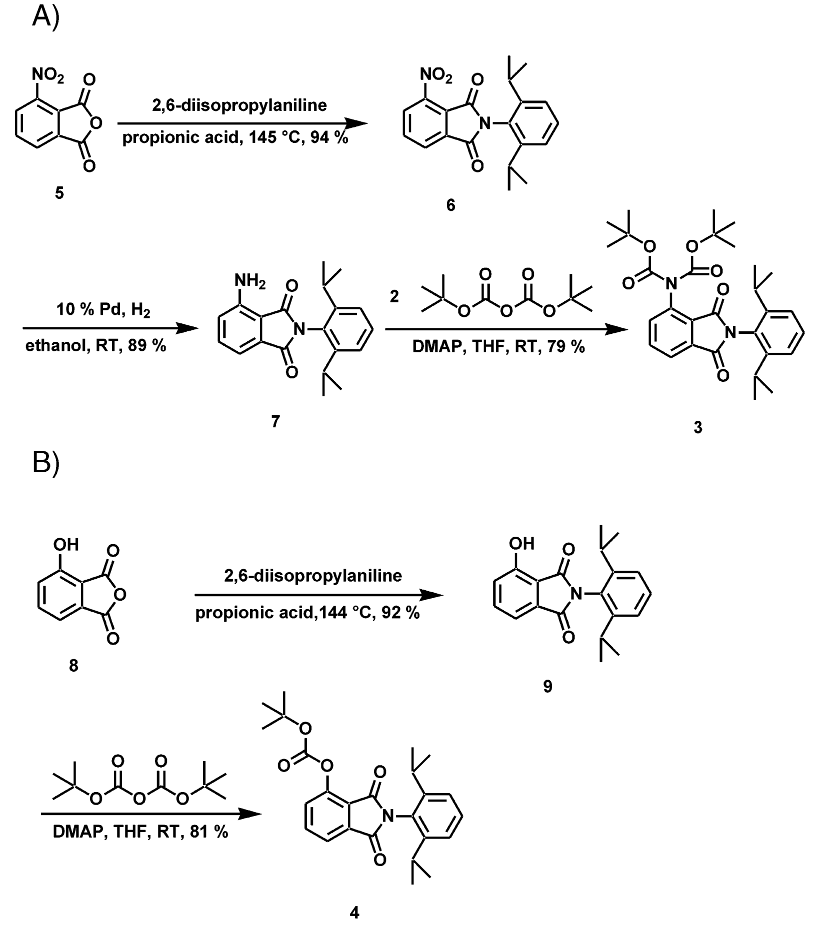
Scheme 2. Synthesis of (A) *N*-(2,6-Diisopropylphenyl)-3-(di-*tert*-butoxycarbonylamino)benzene-1,2-dicarboximide (3) and (B) *N*-(2,6-Diisopropylphenyl)-3-(di-*tert*-butoxycarbonylhydroxy)benzene-1,2-dicarboximide (4)



as eluent, affording 1.28 g (79% yield) of the title compound as a colorless solid: mp 185 °C (dec); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 300 K) $\delta = 7.86$ (d, $^{3}J = 7.3$ Hz, 1 H), 7.75 (t, $^{3}J = 7.6$ Hz, 1 H), 7.47 (d, $^{3}J = 7.9$ Hz, 1 H), 7.40 (t, $^{3}J = 7.3$ Hz, 1 H), 7.21 (d, $^{3}J = 7.6$ Hz, 2 H), 2.59 (sept, $^{3}J = 6.6$ Hz, 2 H), 1.31 (s, 18 H), 1.08 (d, $^{3}J = 6.6$ Hz, 6 H), 1.06 (d, $^{3}J = 6.6$ Hz, 6 H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 300 K) $\delta = 167.70$, 166.51, 150.70, 147.33, 136.72, 135.32, 135.12, 132.85, 130.45, 127.38, 126.94, 124.21, 123.50, 83.78, 29.56, 28.10, 24.33, 24.16; IR (KBr) $\nu = 2974$, 2933, 1802, 1763, 1723, 1614, 1457, 1372, 1276, 1252, 1151, 1115, 1094 cm^{-1}; MS (FD 8 kV) *m*/*z* (rel int) = 522.7 (100) [M^{+}]. Anal. Calcd for $C_{30}H_{38}N_2O_6$: C 68.94, H 7.33, N 5.36. Found: C 68.89, H 7.37, N 5.37.

***N*-(2,6-Diisopropylphenyl)-3-(*tert*-butoxycarbonyloxy)benzene-1,2-dicarboximide (4).** The synthesis was performed as described for **3**. Modifications included the following: 1 g (3.1 mmol) of *N*-(2,6-diisopropylphenyl)-3-hydroxybenzene-1,2-dicarboximide, 80 mL of dry THF, 2.4 g (6.2 mmol) of di-*tert*-butyl carbonate, and 37 mg (0.3 mmol) of 4-*N*,*N*-dimethylaminopyridine. The desired product was purified by column chromatography on silica gel with CH_2Cl_2 as eluent, affording 984 mg (75% yield): mp 173 °C; ^{1}H NMR (300 MHz, CD_2Cl_2, 300 K) $\delta = 7.85-7.83$ (m, 2 H), 7.54−7.47 (m, 2 H), 7.31 (d, $^{3}J = 7.7$ Hz, 2 H), 2.71 (sept, $^{3}J = 6.6$ Hz, 2 H), 1.53 (s, 9 H), 1.15 (d, $^{3}J = 6.6$ Hz, 6H), 1.12 (d, $^{3}J = 6.6$ Hz, 6 H); ^{13}C NMR (75 MHz, CD_2Cl_2, 300 K) $\delta = 167.66$ (C=O), 166.20 (C=O), 150.72, 147.98, 147.74, 136.50, 133.81, 130.64, 128.64, 127.23, 124.38, 123.35, 121.64, 85.31, 29.62, 27.68, 24.06, 23.99; IR (KBr) $\nu = 2970$, 2361, 1769, 1722, 1701, 1615, 1464, 1371, 1277, 1233, 1148, 1116, 1057, 955, 883, 803, 763, 649 cm^{-1}; MS (FD 8 kV) *m*/*z* (rel int) = 422.9 (100) [M+]. Anal. Calcd for $C_{25}H_{29}NO_5$: C 70.90, H 6.90, N 3.31. Found: C 70.83, H 6.91, N 3.40.

3. Results and Discussion

3.1. Synthesis of UV Absorbing Thermochromic Fluorophores. The synthesis of the thermochromic fluorophores **3** and **4** is shown in Scheme 2. The commercially available 3-nitrophthalic anhydride **5** was converted into the corresponding 3-nitrophthalimide **6** by imidization with the sterically demanding 2,6-diisopropylaniline in propionic acid at 145 °C. The 3-nitrophthalimide which was obtained with 3 equiv of amine in 94% yield was hydrogenated in a palladium-catalyzed reaction without further purification. The selective reduction of the nitro group into the amine was achieved with hydrogen and palladium on activated carbon at room temperature in 89% yield. The alkoxycarbonylation of 3-aminophthalimide **7** was obtained in 79% yield by stirring a THF solution of compound **7** with 2 equiv of di-*tert*-butyl dicarbonate at room temperature in the presence of catalytic amounts of 4-(dimethylamino)pyridine.[13] To explore the effect of different donor groups in the benzene nucleus of the phthalimide, we synthesized compound **4**. 3-Hydroxyphthalic anhydride **8** was used as starting material, which was imidized (92% yield) as described for the 3-nitro-

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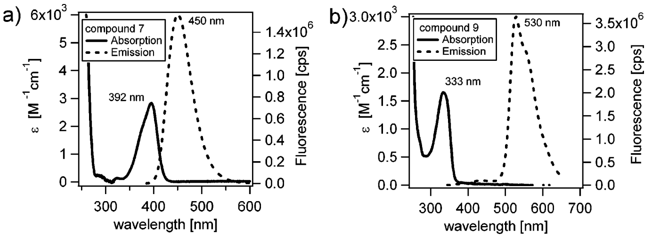

Figure 2. Absorption and fluorescence emission spectra (CHCl$_3$) of (A) compound **7** (emission spectrum recorded at $\lambda_{\mathrm{ex}} = 372$ nm) and (B) compound **9** (emission spectrum recorded at $\lambda_{\mathrm{ex}} = 331$ nm).

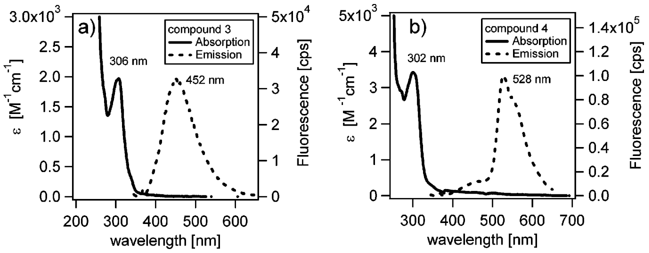

Figure 3. Absorption and fluorescence emission spectra (CHCl$_3$) of (A) compound **3** and (B) compound **4** (both emission spectra recorded at $\lambda_{\mathrm{ex}} =$ 331 nm).

substituted phthalic anhydride. The final alkoxycarbonylation was done in THF with di-*tert*-butyl dicarbonate and 4-dimethylaminopyridine as catalyst in 81% yield.

The absorption bands of the amino- and hydroxy-substituted fluorophore **7** and **9** are broad and structureless, as expected for a charge-transfer transition (Figure 2). These characteristics are in analogy to those of the formerly described 9-aminoperylenedicarboximide **2**.[3] The absorption maximum of **7** and **9** is at 392 and 333 nm, respectively, resulting in essentially colorless fluorophores. The fluorescence of both compounds is quite intense due to intramolecular hydrogen bonds imparting rigidity to the molecule. The fluorescence maximum of **7** is at 450 nm, which leads to an efficient blue emission, whereas the hydroxy-substituted phthalimide **9** has a bigger stokes shift, resulting in a yellow emission (fluorescence maximum at 530 nm).

The absorption spectra of the masked fluorophores **3** and **4** are hypsochromically shifted with respect to **7** and **9**. For **3**, a maximum at 306 nm can be determined, the absorption band of **4** peaks at approximately the same wavelength (302 nm)(Figure 3). The reason for this shift is that the donor groups are no longer in resonance with the π-system of the phthalimide core, due to the electron-withdrawing effect of the acyl groups.[3,14] The deprotected compound **7** exhibits a fluorescence emission peaking at 450 nm with a quantum yield of approximately 0.3. The masked compound **3** is only weakly fluorescing with a roughly 30 times lower quantum yield of 0.01, and the emission spectra of **3** and **7** are very similar. In the case of the deprotected compound **9** and the protected analogue **4**, fluorescence quantum yields of 0.09 and 0.027 were obtained, respectively, again for very similar fluorescence emission spectra peaking at 530 nm. In this case, the deprotected form has a 3 times higher fluorescence quantum yield than the masked compound, corresponding to an acceptable but significantly lower contrast than obtained for the couple **3**/**7**.

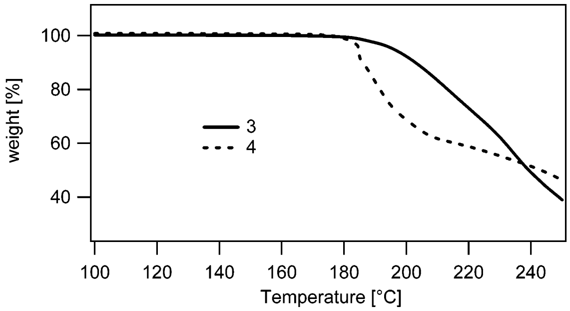

Figure 4. Thermogravimetric analysis of thermochromic fluorophores **3** and **4** as a function of temperature (heating rate 10 °C min^{-1}).

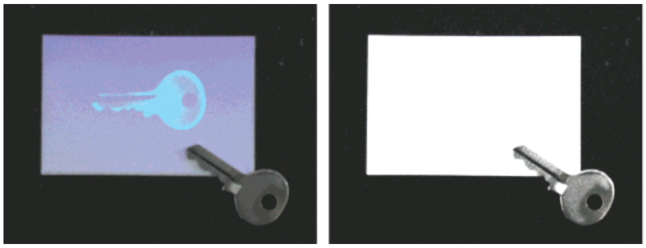

Figure 5. Image of a TLC plate coated with the thermochromic fluorophore **4** after placing a hot metal key onto the plate, recorded with a digital camera: (left) illumination with UV light (wavelength 365 nm) and (right) daylight.

Remarkably, in contrast to compound **1**, the masked fluorophores **3** and **4** have no detectable fluorescence, so that they are invisible under UV light.

The thermal stability of compounds **3** and **4** was investigated by means of thermogravimetric analysis (Figure 4). No clear half-step temperatures can be determined from the graph for the release of carbon dioxide and isobutene, because of the temperatures used in the experiment. In addition to the fragmentation of the alkoxycarbonyl group, a commencing sublimation of the resulting fluorophore takes place. Significant weight loss of the alkoxycarbonylated fluorophore **4** and the twice alkoxycarbonylated fluorophore **3** sets in at around 180 °C in both cases. Compound **4** exhibits a well-developed step, showing a decomposition threshold at 175 °C. Rather, for compound **3**, a transition temperature range (ca. 160−180 °C) is suggested by the graph. The somewhat slower start of the weight loss of compound **3** indicates a slightly higher thermal stability of the carbamate structure in comparison to the carbonic diester structure.

In Figure 5, a silica gel coated TLC (thin-layer chromatography) plate with a thin layer of thermochromic fluorophore **4** is presented. After putting a hot metal key onto the TLC plate an intense solid-state fluorescence of the fragmentated fluorophore in the shape of the key is noticeable under UV light. Under daylight conditions neither the masked nor the fragmentated fluorophore is visible. A similar luminescence increase, resulting in the appearance of a florescence increase where the key had contact with the sample, was observed for compound **4** (data not shown).

Local fragmentation of the thermochromic dyes requires a precise control of the temperature distribution in three dimensions. A practical way to achieve this is by means of

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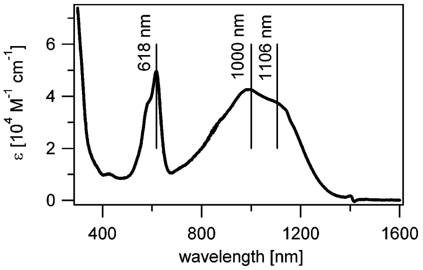

Figure 6. Absorption spectrum of the NIR absorber.

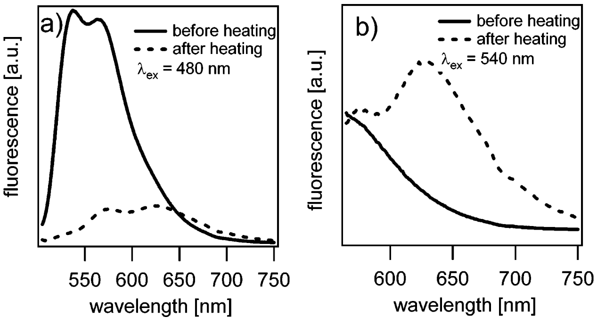

Figure 7. Fluorescence spectra of the film before (dashed line) and after (solid line) heating upon excitation with $\lambda_{\text{ex}} = 480$ nm (A) and $\lambda_{\text{ex}} = 540$ nm (B)

laser-induced heating, due to the ease with which lasers can be focused and scanned through a solid sample.

Here, we provide the proof of principle for such a laser-induced thermal transformation by initiating locally the fragmentation of **1** into **2** in a polymer film. Local heating was achieved by absorption of infrared light (Nd:YAG laser, 1064 nm) by a NIR absorber (see absorption spectrum in Figure 6) included in the film. An important additional property of the NIR absorber we used is its sharp and strong absorption band at 600 nm, which can absorb some fraction of the fluorescence emission of **1**. This allows, by proper adjustment of the concentration ratio of **1** and NIR absorber, compensation for the difference in fluorescence quantum efficiency between **1** and **2**, which are reported in the literature as 0.7 and 0.2, respectively,[15] and obtainment of a clear fluorescence contrast.

In a first experiment, the spectral response of the mixture of **1** and NIR absorber to direct heating was investigated. The samples were heated to (nominally) 200 °C for 2 min; this treatment was expected to lead to complete transformation of **1**. In Figure 7 the fluorescence spectra obtained before and after the heating process are shown.

It can clearly be seen that upon excitation at $\lambda_{\text{ex}} = 480$ nm the as-prepared film exhibits strong fluorescence of **1** in the range $520\ \text{nm} < \lambda_{\text{em}} < 600\ \text{nm}$. A significantly reduced fluorescence is observed for the heated film, showing the band at 640 nm, which is characteristic for **2**, as well as an additional maximum at roughly 570 nm, which is not seen in the spectrum of **2** in solution. One possible explanation of this difference is reaction side products of the decomposition reaction. An off-resonance state of **2** exhibiting fluorescence very similar to that of **1** as reported in literature[14] may provide an alternative explanation. When exciting at $\lambda_{\text{ex}} = 540$ nm, the as-prepared film shows a fluorescence shoulder, whereas a stronger fluorescence intensity, peaking at 640 nm, is visible in the heated film, which is assigned to the fragmentation product **2**. It should be noted that in the absence of the NIR absorber no fluorescence contrast inversion is observed (i.e., the fluorescence of **1** is dominant for all excitation wavelengths). We thus observe a thermally driven color inversion by means of a suitable choice of the absorption and emission bands and the concentrations of the thermochromic chromophore and the NIR absorber.

Laser-induced decomposition of **1** was demonstrated as follows. The sample temperature was preadjusted to 100 °C, a temperature well below the transformation threshold, which lies around 170−180 °C.[3] Local illumination with 1064-nm laser light provided the extra heat necessary for the decomposition of alkoxycarbonyl groups. The fluorescence micrographs obtained from these samples are shown in Figure 8. The anticipated effect is observed; namely, green fluorescence of **1** upon excitation with blue light ($\lambda_{\text{ex}} = 480$ nm) decreases and red fluorescence of **2** upon excitation with green light ($\lambda_{\text{ex}} = 540$ nm) increases where the IR laser light was focused on the sample. Outside the focal spot the fluorescence does not change, confirming that the preheating temperature is well below the threshold for the decomposition of **1**.

This laser-induced transformation brings thermochromic dyes closer to technological applications such as two-color laser marking and optical data storage. In particular, for high-density data storage,[16] where the whole volume of the medium is used, the system presented here bares a number of advantages in comparison to current 3D optical data storage methods. By local heating, binary information could be written in volume elements (voxels) containing the intact form **1** or the fragmented one **2**. Unwanted writing (crosstalk) of neighboring voxels is a severe problem in other proposed data storage schemes like fluorescent dyes that are photobleached in the focus of a laser beam or in two-photon transformation of photochromic molecules.[17] Since local temperature fields can be controlled with high accuracy, due to the well-defined decomposition threshold, crosstalk in the writing procedure should be greatly reduced in a thermochromic system. Furthermore, since the write and read processes are based on different physical processes (thermal decomposition and fluorescence excitation with visible light, respectively), the probability of unwanted writing by the read-out is minimized. Importantly, the fluorescence contrast between pristine and heated material allows determination of whether transformation has taken place both by reduced fluorescence upon excitation at 480 nm and by increased fluorescence upon excitation at 540 nm. The 75-min sample has some fluorescing impurities that are probably dust particles and would be problematic in a data storage application. They give a neat illustration of the advantage

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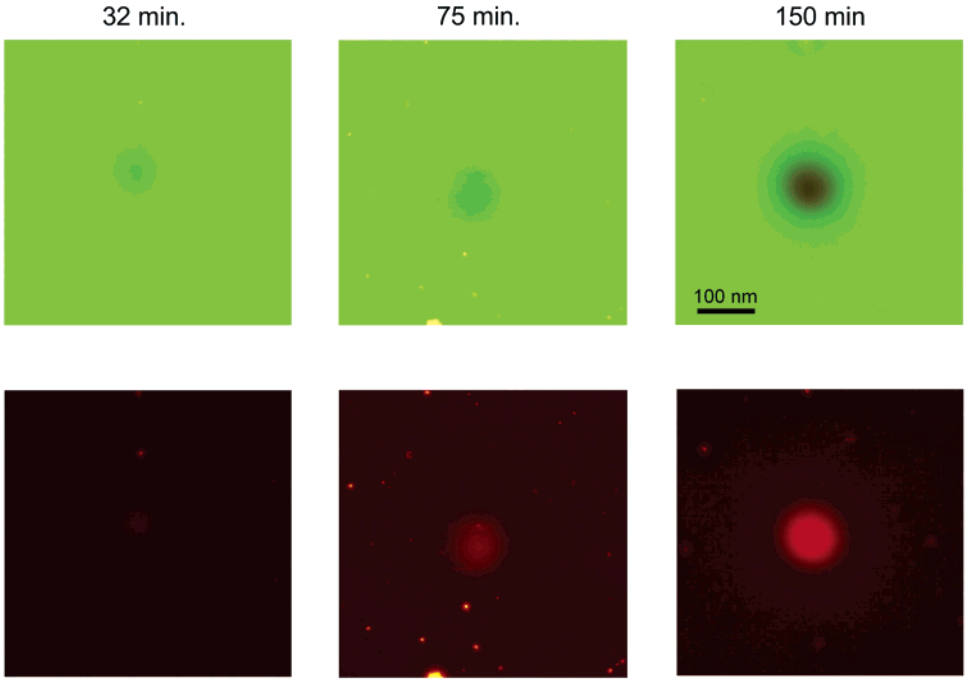

Figure 8. Fluorescence micrographs upon excitation of the fluorescence with $\lambda_{ex} = 480$ nm (upper row) and $\lambda_{ex} = 540$ nm (lower row) for different exposure times to the NIR laser. The sample temperature was preadjusted to 100 °C.

of redundant information: they show up as bright spots for both excitation wavelengths and can therefore be easily differentiated from areas where genuine information was stored. This two-fold redundant read-out scheme greatly reduces the probability of errors and should therefore allow for an increased information density.

It should be pointed out that although the times required for the laser-induced transformation in the experiment presented here are on the order of half an hour, they could be considerably reduced by increasing the local temperature in the NIR laser spot, e.g., by means of a tighter focusing, higher laser intensity or matrix and substrate materials with lower heat conductivities. Thus, local transformation induced by the temperature rise and subsequent heat diffusion after a single short laser pulse is possible.

Conclusions

In conclusion, the efficient synthesis of alkoxycarbonylated 3-amino- and 3-hydroxy-substituted phthalimides **3** and **4** provides the first thermochromic fluorophores in which the absorption bands of the masked and fragmentated form are exclusively located in the invisible UV region. The masked form has in both cases a fluorescence quantum yield that is significantly reduced compared to the fragementated form. The generated thermochromic fluorophores are promising candidates for durable, invisible imprintings of plastics. Furthermore, it was demonstrated that the laser-induced local heating via a NIR absorber can be used to induce the thermal decomposition. The local change in absorption envisages two-color laser marking applications. Owing to an adequate combination of the emission and absorption bands of the 9-aminoperylenedicarboximide and the NIR absorber, fluorescence signals with inverted contrast can be obtained by selecting different excitation wavelengths. This provides redundant and therefore highly reliable readout of written information. Thus, this system offers a data-storage alternative to the technologically demanding two-photon technology where the advantages of redundant data recovery by two-color read-out have already been pointed out.[18]

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