An excimer emission approach for patterned fluorescent imaging

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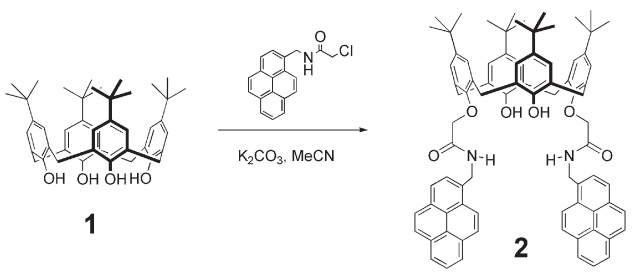
Selective removal of t-Boc protecting groups in a polymer film imbedded, pyrene-containing calixarene derivative results in the generation of a patterned fluorescence image without employing wet developing processes.

Generation of patterned images in polymer films has been extensively studied and used in the context of fundamental and applied research.[1–9] The general strategy most often employed to create patterned functional images in polymer films relies on a "two-step procedure." First, reactive functional groups, such as amines, carboxylic acids, and alcohols, are produced by photo-induced chemical transformations of substrates in exposed areas of polymer films. The reactive groups, formed in this manner, then undergo covalent, ionic, or hydrogen bonding interactions with functional dyes that are applied to the exposed films (wet processing). However, this procedure has several potential limitations that arise from difficulties with dye penetration into polymer matrices and the long-term instability of patterned images when dye molecules are bound through weak ionic or hydrogen bonding interactions.

In order to overcome the intrinsic problems associated with images formed by using the typical two-step procedures, we[10–12] and others[13–17] have developed alternative, direct methods for generating color or fluorescence images in polymer films that do not require the use of wet-development techniques. Below, we describe a new, direct approach to patterned fluorescence imaging in polymer films, which relies on an acid promoted transformation of excimer to monomer emission in a bis-pyrene containing 4-*tert*-butylcalix[4]arene.

The construction of the molecular framework for this new imaging technique employs 4-*tert*-butylcalix[4]arene (**1**, Scheme 1) as a template for holding two pyrene moieties in relatively close proximity. Two pyrene chromophores are covalently bonded to the lower rim of the calixarene by the reaction of **1** with *N*-(1-pyrenylmethyl)chloroacetamide, NaI and K_2CO_3 in acetonitrile.



Scheme 1 Preparation of pyrene-containing calixarene **2**.

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NMR spectroscopic analysis indicates that the bis-pyrenylcalixarene **2** exists in a cone conformation. Evidence for this assignment comes from the observation of doublets at *ca.* 2.6 and 2.4 ppm in the ^{1}H NMR spectrum and a single resonance at *ca.* 32 ppm in the ^{13}C NMR spectrum. Interestingly, bis-pyrenylcalixarene **2** does not have a typical pyrene excimer fluorescence emission band at 470 nm. Instead, **2** strongly emits in the 350–400 nm region, characteristic of monomeric pyrene fluorescence. The absence of excimer fluorescence indicates that the two pyrene moieties in **2** are not orientated in a face-to-face manner required for excimer formation.

In order to gain more insight into the conformation of bis-pyenylcalixarene **2**, its X-ray crystal structure was determined.† The structure clearly demonstrates that the two pyrene groups in **2** do not exist in a face-to-face orientation (Fig. 1, left) but, instead, that they are bent away from each other. Careful analysis of the crystallographic data reveals that two distinct kinds of intramolecular hydrogen bonds are responsible for the dispositions of the pyrene moieties. Specifically, amide hydrogens form intramolecular hydrogen bonds with oxygens of neighboring phenolic hydroxyl groups in the calixarene ring. In addition, the phenolic hydrogens are hydrogen bonded to oxygens on neighboring phenol ether groups. These H-bonding interactions combine to orient the pyrene groups away from each other. A similar observation has been described for a *tert*-butylcalix[4]arene bearing two ferrocenyl amide groups.[18]

Based on this structural information, we hypothesized that placement of *tert*-butyloxycarbonyl (t-Boc) groups on the free phenolic hydroxyl moieties in **2** would block the intramolecular hydrogen bonding interaction responsible for the preferred conformation of **2**. If this proposal is correct, t-Boc protection should result in restoration of the pyrene–pyrene interactions. (Fig. 1, right).

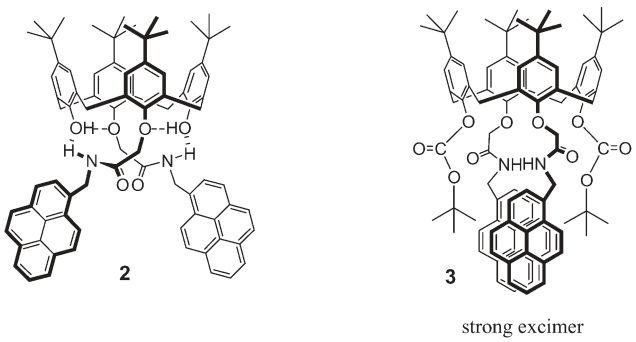

Fig. 1 Structure of the pyrene-containing calixarene **2**, deduced from X-ray crystallographic analysis (left), and modeled t-Boc-protected derivative **3** (right).

In order to test this proposal, the t-Boc protected bis-pyrenylcalixarene **3** was prepared.‡ As proposed, the fluorescence spectrum of **3** contains a strong pyrene excimer emission band at 470 nm and a weak monomer band as shown in the 350–400 nm region (Fig. 2). The observation of strong excimer fluorescence, suggests that **3** preferentially exists in a conformation where the t-Boc groups are oriented outward so as to allow π–π stacking interactions between the pyrene moieties.

The results presented above give rise to an intriguing strategy for fluorescence imaging design. Accordingly, removal of the t-Boc groups in **3** would be accompanied by the disappearance of the pyrene excimer fluorescence and concomitant production of monomer fluorescence in the 350–400 nm region. Furthermore, if t-Boc elimination could be promoted in selected areas of a polymer film, patterned fluorescence images would be formed. This reasoning leads to a strategy for fluorescence imaging in which fluorescence changes are promoted by chemical amplification (CA) processes.[19–21] Specifically, in the post-exposure bake (PEB) step, a catalytic amount of acid produced by irradiation of a photoacid generator (PAG) present in the polymer film would induce a chemical reaction cascade involving acid-catalyzed deprotection of t-Boc groups of bis-pyrenylcalixarene **3**.

To test this strategy, a dioxane solution containing poly(methyl methacrylate) (PMMA) (79 wt%), t-Boc-protected bis-pyrenylcalixarene **3** (20 wt%), and the photoacid generator, triphenylsulfonium hexafluoroantimonate (TPSHFA) (1 wt%), was spin-casted on a silicon wafer. The resulting thin film was exposed to photomasked UV light for 60 s. After irradiation, the film was subjected to post-exposure bake (PEB) at 120 °C for 60 s. As the fluorescence microscope imaging results in Fig. 3 show, a patterned fluorescence image is produced. The bright areas (pale blue in color format) are areas exposed with UV light while the dark areas (dark blue in color format) represents unexposed areas.§

This effort has led to the development of a new method for generating patterned fluorescent images in polymer films. The technique takes advantage of a change in fluorescence properties caused by photoacid promoted reaction of the readily prepared calixarene derivative **3** which contains two pyrene groups connected to a phenol t-Boc protected calixarene. The pyrene groups in **3** are oriented face-to-face and, as a result, they give rise to strong excimer fluorescence. Photoacid induced removal the t-Boc protecting groups from **3** generates **2**, in which intramolecular hydrogen bonding interactions cause a distant orientation of the pyrene moieties and monomer fluorescence predominantly. We have used these unique structural and photophysical properties to design a novel system for patterned fluorescence imaging in polymer films that does not require wet developing processes. The exciplex based imaging methodology described in this report should significantly add to the knowledge base of the areas of science that focus on the development of patterned functional images in the polymer film.

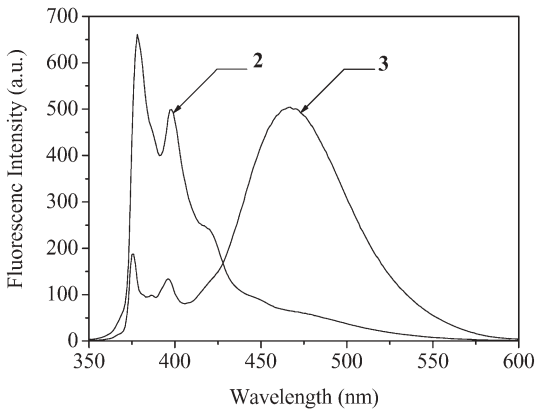

Fig. 2 Fluorescence emission spectra of **2** and **3** (6 μM) in CH_3CN (excitation 343 nm).

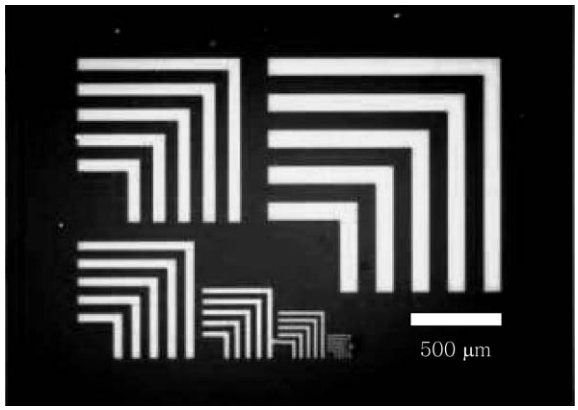

Fig. 3 Fluorescence microscope imaging patterns obtained from photomasked irradiation of a *ca.* 1.0 μm-thick PMMA film containing the **3** and TPSHFA on a silicon wafer followed by PEB processing. The dark areas are the photomasked areas.

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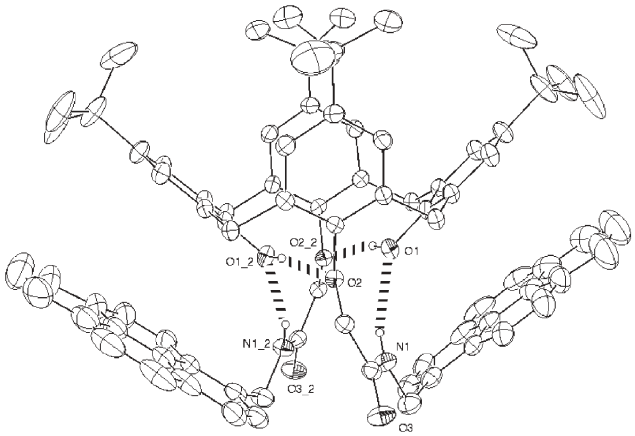
Notes and references

† *Crystal data for* **2**: Crystals of **2** were obtained by slow evaporation of the methylene chloride solution. All X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of 29 reflections in the range $10.0^\circ < 2\theta < 25.0^\circ$. Absorption corrections were not made. A brown crystal of **2**, shaped as a block of approximate dimensions 0. 44 × 0. 40 × 0. 36 mm, was used to collect crystal diffraction intensity data. Unit-cell parameters and systematic absences indicated two possible space groups: *Cc* and *C*2/*c*. The structure analysis converged only in *C*2/*c*. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The O–H and N–H hydrogen atoms were located and refined isotropically, and the remaining hydrogen atoms were generated in ideal positions and refined in a riding mode.$C_{82}H_{84}N_2O_7$, M = 1209.51, a brown block, 0. 44 × 0. 40 × 0. 36 mm, monoclinic, space group *C*2/*c*, a = 31.215(4) Å, b = 12.941(3) Å, c = 19.891(3) Å, β = 120.008(7)°, V = 6958(2) Å^3, Z = 4, D_c = 1.155 g cm^{-3}, $F(000)$ = 2584, T = 293(2) K, 6137 reflections collected, 6020 unique, R_1 = 0.1012, wR_2 = 0.2783, final R indices [$I > 2\sigma(I)$], data/restraints/parameters = 3153/0/418. CCDC 263455. See http://www.rsc.org/suppdata/cc/b5/b501568e/ for crystallographic data in CIF or other

electronic format.



‡ *Preparations:* **2**: Under nitrogen, a solution of *tert*-butylcalixarene 1 (1.00 g, 1.54 mmol), *N*-(1-pyrene-methyl) chloroacetamide (1.0 g, 3.25 mmol), K_2CO_3 (0.23 g, 1.69 mmol), and a catalytic amount of sodium iodide in 50 mL of acetonitrile was stirred at reflux for 24 h, cooled to room temperature and concentrated *in vacuo*, giving a yellow solid. Water (50 mL) and CH_2Cl_2 (100 mL) were added, and the organic layer was separated, washed with water (3 × 50 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo* to give a solid, which was crystallized (1:9 methylene chloride–diethyl ether (1:9) to yield 1.2 g (68%) of 1 as a yellow solid, mp: 267–268 °C. IR (KBr, cm^{-1}): 3406, 1670. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.62 (broad t, 2 H, NH), 8.38–7.58 (m, 18 H, Ar–H, pyrene), 6.28 (s, 4 H, Ar–Hm), 6.19 (s, 4 H, Ar–Hm), 5.41 (s, 4 H, $ArOCH_2$), 5.21 (s, 2 H, ArOH), 4.04 (d, 4 H, $NHCH_2$, pyrene, J = 2.59 Hz), 2.61 (d, 4 H, $ArCH_2Ar$, J = 13.19 Hz), 2.4 (d, 4 H, $ArCH_2Ar$, J = 13.19 Hz), 1.04 (s, 18 H, Ar–t-bu), 0.66 (s, 18 H, Ar–t-bu). ^{13}C NMR (50 MHz, $CDCl_3$): 169.4, 149.2, 148.9, 148.4, 142.3, 132.4, 129.2, 126.5, 126.3, 125.3, 34.3, 32.4, 31.5 ppm. Anal. Calcd. for $C_{82}H_{82}N_2O_6$: C, 85.66; H, 6.94. Found: C, 85.68; H, 6.91. **3**: Under nitrogen, a solution of **2** (1.0 g, 0.84 mmol), t-BOC anhydride (0.08 g, 2.52 mmol) and NaH (0.06 g, 2.5 mmol) in 100 mL of THF were stirred at reflux for 24 h, and concentrated *in vacuo* to give a yellow solid. CH_2Cl_2 (100 mL) and water (50 mL) were added, and the organic layer was separated, washed with water (3 × 50 mL), dried over anhydrous $MgSO_4$, and concentrated *in vacuo* to give a residue which was subjected to column chromatography on silica gel (EA/HX) to yield 1.2 g (66%) of **3** as a solid, mp: 227–228 °C; IR (KBr pellet, cm^{-1}): 3312 (–NH), 1720 (CO). ^{1}H NMR (200 MHz; $CDCl_3$): δ 9.18 (t, 2 H, NH), 8.34–7.69 (m, 18 H, Ar–H, pyrene), 7.18 (s, 4 H, Ar–Hm), 6.62 (s, 4 H, Ar–Hm), 5.42 (d, 4 H, $NHCH_2$ pyrene, J = 5.79 Hz), 4.37 (s, 4 H, $ArOCH_2CO$), 4.20 (d, 4 H, $ArCH_2Ar$, J = 12.99 Hz), 3.29 (d, 4 H, ArCH2Ar, J = 12.39 Hz), 1.34 (s, 18 H, O–t-bu), 1.00 (s, 18 H, Ar–t-bu), 0.86 (s, 18 H, Ar–t-bu); ^{13}C NMR ($CDCl_3$): δ 178.2, 170.0, 149.4, 140.3, 134.5, 133.0, 132.7, 132.6, 131.8, 128.5, 126.0, 124.8, 76.7, 47.9, 31.9, 25.4, 11.6 ppm. Anal. Calcd. for $C_{92}H_{98}N_2O_{10}$: C, 79.40; H, 7.10. Found: C, 79.36; H, 7.11.

§ *Fluorescence Imaging*: A solution containing **3** (19 wt%), poly(methyl methacrylate) (PMMA) (80 wt%), and the photoacid generator, triphenylsulfonium triflate (1 wt%), in 1,4-dioxane (2 mL) was filtered through a 0.2-μm membrane filter and spin-coated at 3,000 rpm for 45 s followed by a prebaking at 120 °C for 30 s. The prebaked plate was exposed to photomasked 254 nm-UV light for 30 s followed by PEB at 120 °C for 60 s. The fluorescent image pattern was photographed by using a fluorescence microscope.

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