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Light-Responsive Polystyrene Films Doped with Tailored Heteroaromatic-Based Fluorophores

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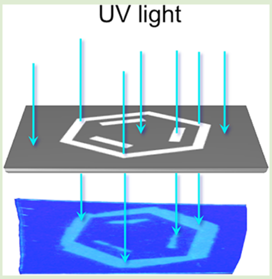
Supporting Information

ABSTRACT: We describe a simple but effective strategy for imparting light-responsive peculiarity to polystyrene films. A pH-sensitive fluorescent dye having the electron-poor pyridine nucleus as a key structural feature was synthesized and dispersed at low loadings (0.2−0.5 wt %) in a PS matrix. Once light irradiation in the near-UV range was sent to PS/dye films, PS photooxidation likely occurred at the film surface with the formation of carboxylic compounds. These species locally promoted dye protonation, thus, yielding a clear change of the film emission from blue to green. This study opens the door to a wide range of light-responsive materials from easily accessible polymers, enabling the use of UV light as an effective trigger for smart materials and devices.



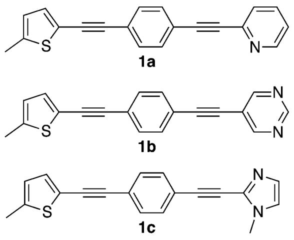
In the last years, impressive interest has been devoted to the research of chromogenic polymers, which are capable of responding to various stimuli (e.g., light, heat, mechanical stress, and chemical stimuli) through a macroscopic optical output.[1−4] The energy of the stimulus is properly transduced into optical variations (i.e., absorption, emission, refractive index) as a function of external interference. This mechanism allows the preparation of "smart" devices for many different applications, such as anticounterfeiting systems, attoreactor sensors, and informational displays.[5−7] Soft intelligent materials are based on the assembly of different units performing specific functions; for example, organic or inorganic chromophores such as dyes with available delocalized electrons or metal derivatives constitute the basis of the sensor mechanism since they confer to the material a variation of the opto-electronic features in reaction to a stimulus. These responsive compounds can be inserted within polymeric matrices (either in interfacial regions or in more complex supramolecular architectures) to obtain highly tunable platforms.[8]

As far as physical stimuli are concerned, light-irradiation is, indeed, eminent in responsive polymer systems.[9−11] Chromogenic materials, in which a photochemically induced change in the structure causes a significant alteration of the optical features, have been also worthwhile in the development of optical filters and optical data storage media.[10]

In the design of innovative and even more attractive smart polymer systems, we present herein the realization of light-responsive atactic polystyrene (PS) films, which contain moderate amounts (≤0.5 wt %) of a heteroaromatic pH-sensitive fluorescent probe. When polystyrene is subjected to light irradiation near the UV region and in the presence of air, it undergoes photooxidation, yielding hydroperoxy, hydroxyl, and carbonyl group formation, especially near the surface layer.[12,13] The formation of carboxylic moieties flanked by the release of protons during the reaction between singlet oxygen and PS favors dye protonation and converts film emission only on the region subjected to illumination.

Organic chromophores, usually based on extended π-conjugated structures, show large photoresponses in a spectral region that can be easily tuned from the visible to the near-infrared by appropriate molecular design. Furthermore, those featuring heteroaromatics as the main π-conjugated backbones usually display increased stability and thermal and chemical robustness required for the fabrication of plastic materials. In particular, thiophene-based π-conjugated molecules have attracted great interest due to their remarkable electric and optic features.[14−16] Starting from these observations, in this study we focused our synthetic efforts on the preparation of novel 1,4-bis-ethynylbenzenes **1a−c** (Scheme 1) bearing the

Scheme 1. Chemical Structures of Compounds 1a−c



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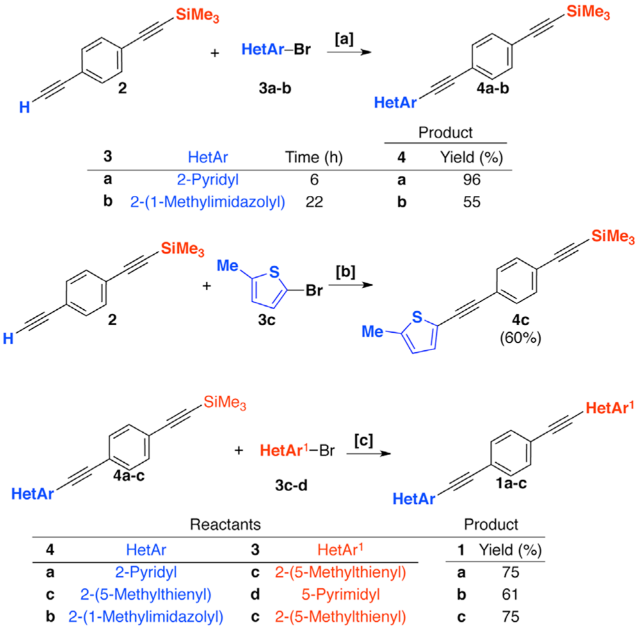
electron-poor pyridine and pyrimidine cores or the electron-rich 1-methylimidazole nucleus as pH sensitive moieties Fluorophores **1a**−**c** have been easily prepared according to a simple and scalable synthetic procedure involving two sequential palladium-catalyzed selective alkynylation reactions of [(4-ethynylphenyl)-ethynyl]trimethylsilane (**2**)[17] (Scheme 2).

Scheme 2. Synthesis of Compounds 1a−c[a]



3	HetAr	Time (h)	4	Yield (%)
			Product	
a	2-Pyridyl	6	a	96
b	2-(1-Methylimidazolyl)	22	b	55

Reactants				Product	
4	HetAr	3	HetAr^1	1	Yield (%)
a	2-Pyridyl	c	2-(5-Methylthienyl)	a	75
c	2-(5-Methylthienyl)	d	5-Pyrimidyl	b	61
b	2-(1-Methylimidazolyl)	c	2-(5-Methylthienyl)	c	75

[a]Reagents and conditions: [a] $PdCl_2(PPh_3)_2$ (5 mol %), CuI (6 mol %), Et_3N, 80 °C. [b] $PdCl_2(PhCN)_2$ (5 mol %), *t*-Bu_3P (10 mol %), DABCO (2.0 equiv), MeCN (1M), RT, 18h. [c] $PdCl_2(PhCN)_2$ (5 mol %), *t*-Bu_3PHBF_4 (10 mol %), CuI (10 mol %), $BnBu_3NCl$ (20 mol %), toluene, $NaOH_{aq}$, 40 °C, 18h.

In detail, trimethylsilylalkynes **4a**,**b** were obtained in a 96 and 55% isolated yields, respectively, from a palladium- and copper-catalyzed classical Sonogashira reaction involving **2** and heteroaryl bromides **3a**,**b**.[18] The thienyl-containing trimethylsilylalkyne **4c** was prepared by a Cassar-Heck alkynylation of **2** with 2-bromo-5-methylthiophene (**3c**) as recently described by us.[17] The trimethylsilylalkynes **4a**−**c** so obtained were then reacted with heteroaryl bromides **3c**,**d** according to our recent protocol for the Pd- and Cu-catalyzed Sila-Sonogashira cross-coupling under phase-transfer conditions,[19] allowing the isolation of the required pH-sensitive chromophores **1a**−**c** in 61−75% yields.

All of the chromophores show absorption maxima in the near-UV region, mostly centered at 340 nm (Table 1). Looking at the emissions, compound **1a** displays both the largest Stokes shift (68 nm) and the highest quantum yield (QY = 0.20), thereby making it suitable as a possible candidate for the preparation of materials with optical response to external stimuli.[17]

Table 1. Optical Characteristics of the Prepared Dyes Dissolved in THF

dye	absorption (λ_{max} [nm]; ε [M^{-1} cm^{-1}])	emission (λ_{max} [nm]; QY)
1a	338; 40000	404; 0.20
1b	339; 45000	403; 0.17
1c	340; 34000	377; 0.15

On the other hand, the QY of the imidazole-based chromophore **1c** was judged too low to be useful for this study.

Polystyrene (PS)/**1a** films were prepared by dissolving PS and the 0.2−0.5 wt % of **1a** in $CHCl_3$. After evaporation of the solvent, the blends were compression molded at 160 °C for 5 min into thin films of about 200 μm of thickness. All PS/**1a** films showed emission features (excitation maxima between 370 and 380 nm) almost identical in their form, with fluorescence maxima centered in the range between 410 and 430 nm, about 20 nm red-shifted in comparison to those observed in toluene. The fluorescence appears also less structured than that recorded in solution. Noteworthy, no emission bands attributed to the generation of supramolecular chromophoric aggregates were detected in the range of concentration investigated.

When PS/**1a** samples were subjected to multiple excitation experiments at 300 nm, the irradiated region of the film experienced a chromogenic behavior by changing the color of the emitted light from blue to green after 30 scans. This phenomenon was due to the progressive red shift of the **1a** emission band from 420 to about 460 nm as a function of the number of excitation scans (Figure 1).

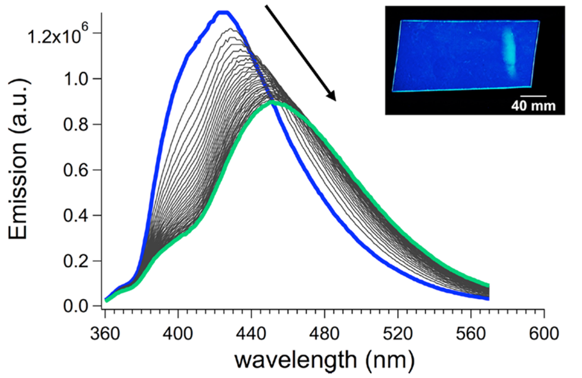


Figure 1. Emission spectra (λ_{exc} = 300 nm) of a 0.5 wt % PS/**1a** film as a function of the excitation scans and (inset, (λ_{exc} = 366 nm)) image of the film with the green line due to light irradiation after 30 scans.

It was noted that the phenomenon appeared much less evident by exciting at 355 nm (Figure S1), that is, by using a wavelength close to the excitation maximum of **1a** in PS (370−380 nm). In fact, only a red shift of 20 nm was recorded for a number of scans greater than or equal to 30. This clearly indicates that higher excitation energy is required to rapidly and effectively change the fluorescence of PS/**1a** films. As a matter of fact, if a more powerful UV radiation is utilized, a prompt (about 5 times faster) chromogenic phenomenon occurs (Figure 2). Also, the emission band after UV irradiation appears about 20 nm more red-shifted than pristine film (from 420 to 480 nm), thus, suggesting a more efficient and complete process.

The small differences in the shape of the emission band depicted in Figures 1 and 2 for pristine films can be likely attributed to different dye arrangements formed within the solid PS matrix.[20]

The above-described optical effect in PS was also observed for **1a** in organic solution at different pH. In the analysis of pH-dependent properties, the absorption and emission spectra of

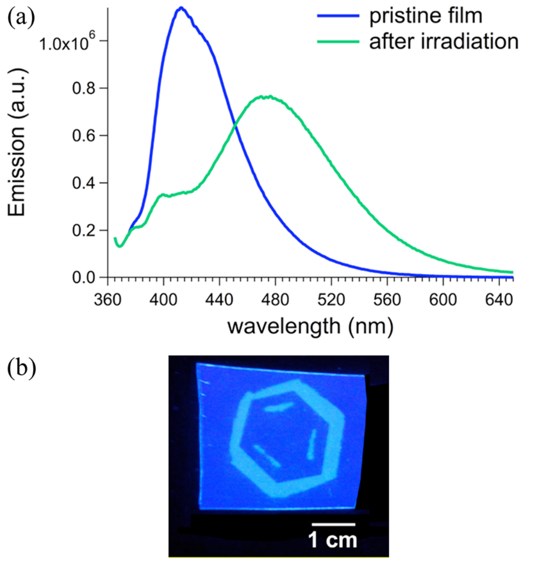


Figure 2. (a) Emission spectra (λ_{exc} = 300 nm) of a 0.5 wt % PS/**1a** film before and after irradiation with a high pressure Hg UV lamp for 5 min; (b) image of the same film after the UV lamp irradiation through a paper mask depicting the Kekulè structure of benzene, taken under the excitation at 366 nm.

1a were recorded in THF (or in EtOH/water mixture (4/6 v/v)) between pH 2.0 and 8.0 using HCl 0.1 M or NaOH 0.1 M for pH adjustment. Under acid conditions, the emission band at 404 nm experienced a red shift to a broad and almost structureless fluorescence pointed at 520 nm. The pK_a value, determined also by potentiometric titration, was found to be 4.8, which is comparable to typical pK_a of pyridine derivatives. The pyrimidine derivative **1b**, which displays a QY comparable to **1a**, was discarded for further analysis due to its lower basicity (pK_a about 1.2).

The existence of a well-defined isosbestic point centered at 460 nm clearly indicated the presence of two states assigned to the protonated and the neutral forms of **1a**. The pH-dependent properties were also recorded in organic media, such as $CHCl_3$ and toluene, by titration with trifluoroacetic acid (TFA, pK_a = 0.23) and camphorsulfonic acid (CSA, pK_a = 1.2), respectively. In toluene, the emission spectra of **1a** shows a decrease of the emission band at 404 nm with increasing CSA concentration (Figure 3a) and a simultaneous increase of the emission at 475 nm, also giving rise to an isosbestic point at 430 nm. Both isosbestic point and fluorescence attributed to the protonated form **1a** resulted more than 30 nm blue-shifted with respect to the emission features recorded in THF. Nevertheless, **1a** shows a distinct chromogenic behavior even in a less polar organic medium, such as toluene, by changing the color of the solution from blue to green at the end of the titration with CSA (Figure 3b).

These results suggest that the color change that occurred for PS/**1a** films under irradiation is likely due to the protonation of the pyridine ring of **1a**.

It has been reported that when PS is subjected to light irradiation near the UV region and in the presence of air, it undergoes photooxidation, yielding hydroperoxy, hydroxyl, and carbonyl group formation, especially near the surface layer.[12,21] The initiation of photochemical reactions in PS includes an initial act of absorption of a quantum of light by a macromolecule or by an impurity present in the polymer. Because pure PS does not absorb UV light above 290 nm, the initiation process may be ascribed to the formation of charge-transfer complexes between PS and molecular oxygen, which absorbs at wavelengths higher than 300 nm. However, one of the main causes of polymer photooxidation is the formation of singlet oxygen by energy transfer to molecular oxygen from excited external chromophoric impurities present in commercial PS.[13] These trace amounts of impurities may include initiator fragments and residual radicals with oxygen produced during polymerization and trapped within the polymer matrix. During the initiation stage of photodegradation, where PS benzylic macroradicals are readily generated, peroxy radicals and hydroperoxide groups are produced, which decompose in the propagation steps, yielding carbonyl compounds, comprising carboxylic derivatives.[21]

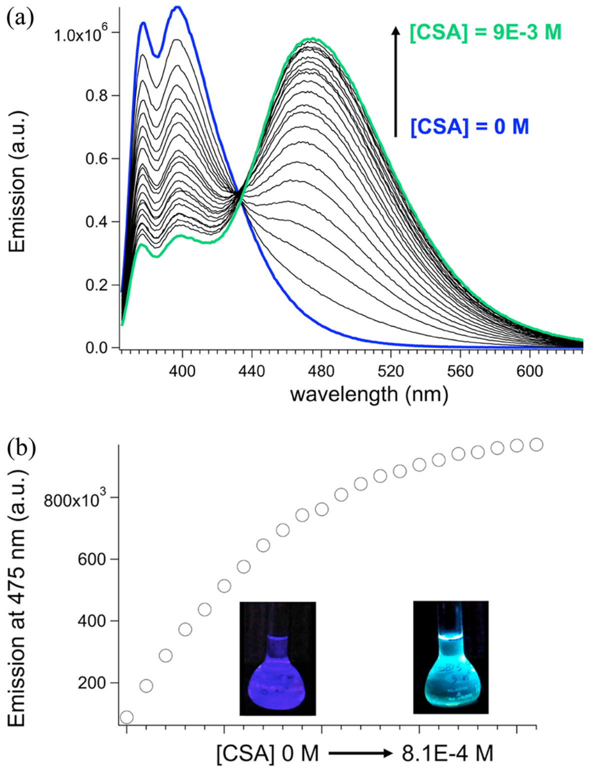


Figure 3. (a) Spectrofluorimetric titration of 10^{-5} M **1a** toluene solution with 10^{-2} M CSA toluene solution (λ_{exc} = 355 nm); (b) titration emission spectra of **1a** and (inset) images of the solution fluorescence at the beginning (left) and at the end (right) of the titration (λ_{exc} = 366 nm).

The same excitation experiments were then repeated starting from PS/**1a** films prepared from purified PS matrix (p-PS), obtained after a double cycle of dissolution in $CHCl_3$ and precipitation in MeOH. It is worth noting that the excitation spectrum of the p-PS shows a strong reduction of the overall emission with respect to pristine PS, most evidently in the range 300−360 nm (Figure S2). At the end of the experiment, the p-PS/**1a** film showed only a reduction of the emission intensity of about 20%, a phenomenon that recalls dye photobleaching (Figure 4). This indicates that the presence of impurities or PS additives that interact with light at 300 nm and oxygen appears fundamental for the occurrence of the chromogenic phenomenon.

Similar results were also obtained by analyzing PS/**1a** films in the absence of oxygen. The films were excited at 300 nm within a quartz cuvette under a nitrogen atmosphere. In this case, a 7%

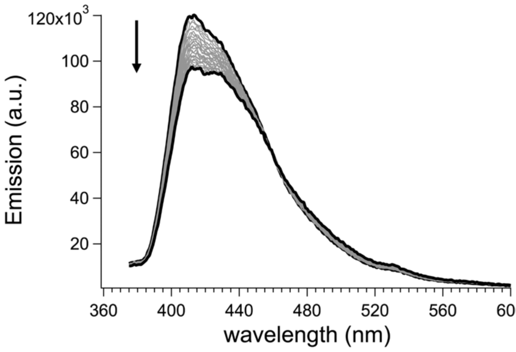


Figure 4. Emission spectra (λ_{exc} = 300 nm) of a 0.5 wt % p-PS/**1a** film as a function of the excitation scans (30 scans).

reduction of the emission intensity was merely recorded, without the formation of the fluorescence contribution near 470−480 nm.

The isolation of these chromophoric impurities by selective extractions is always affected by the presence of noteworthy amounts of low molecular weight oligomers of PS. Considering the large amount of additives comprised in a polymer matrix, the identification of the exact chemical specie (or species) able to initiate PS degradation is still a challenge.[22]

Notwithstanding, the light-responsive behavior also takes place in p-PS/**1a** films when a stronger UV source (high pressure Hg lamp) is utilized. In this case, the initiation step is attributed to the excitation of benzene rings to singlet and triplet states, followed by reactions giving free radical formation by bond scission.[12]

Because **1a** is optically stable under UV excitation when dissolved in THF or toluene (Figure S3), the chromogenic behavior may be likely attributed to the protonation of dye molecules by carboxylic compounds generated during light irradiation at 300 nm or by the UV lamp. The detection of trace amounts of carboxylic groups in those confined and thin areas were not completely accessible by means of ATR/FTIR investigations. Experiments performed on the irradiated film portions evidenced only moderate evolutions in the 1650−1780 and 3100−3600 cm^{-1} regions, which correspond, respectively, to the domains of C═O and OH stretching vibrations (Figure S4).

An efficient alternative to confirm our hypothesis consisted of mixing 1 wt % of 1,4-diazobicyclo[2.2.2]octane (Dabco, pK_a = 8.7) within the PS/**1a** mixture, thus, using an aliphatic base stronger than **1a**. This amine can react with the released carboxylic compounds during light excitation instead of **1a** molecules. Accordingly, during excitation at 300 nm of PS/**1a** Dabco films, only a modest photobleaching occurred, without the formation of emission features above 450 nm (Figure S5).

The emission coming from pristine and irradiated portions of PS/**1a** films was also analyzed by lifetime experiments (Figure S7). PS/**1a** films before irradiation at 300 nm were characterized by average lifetime parameters of 0.32 (41% population), 0.64 (53% population), and 1.59 ns (6% population). After irradiation (30 scans), the same film showed that lifetime parameters changed toward longer-lived emission, that is, 0.32 (25% population), 0.77 (69% population), and 1.73 ns (6% population). It is worth noting that these values are intermediate between those calculated for **1a** and for **1a** in the protonated form by CSA, that is, 0.43 (31% population), 0.91 (62% population), and 2.3 ns (7% population). This result agrees well with the hypothesis that only the PS/**1a** layer exposed to the film surface is interested by the light irradiation. In other words, only a fraction of **1a** dispersed within PS is affected by the chromogenic behavior. Accordingly, lifetime parameters calculated from the emission collected from the inner layers of PS/**1a** film (0.31 (30% population), 0.69 (62% population), and 1.56 ns (8% population)) fit well with those of pristine PS/**1a** films.

Finally, the reversibility of the chromogenic phenomenon was also tested, by exposing the PS/**1a** film in a NH_3-saturated air atmosphere (pK_a ammonia = 9.25) at 20 °C (Figure S6). After 30 min, the irradiated portion of the film reversed its color from green to blue, restoring the typical emission coming from deprotonated **1a** chromophores. This result strengthens our hypothesis that color switching is determined by the generation of carboxylic compounds during UV irradiation.

In conclusion, the phenomenon described in the present paper suggests an interesting strategy for the realization of light-responsive plastic films by means of a simple but effective and scalable procedure. Once the pH-sensitive chromophore is prepared, it can be readily dispersed into a commodity plastic such as PS. The chromogenic phenomenon occurs rapidly when a light irradiation in the near-UV range hits the film surface in the presence of oxygen. The color change is connected with dye protonation caused by the release of carboxylic compounds from the photooxidized PS matrix.

Further study is in progress to extend the discovery to other polymeric materials and dyes (i.e., on passing to imidazole derivatives) to better modulate the luminescent response to external stimuli. Analogous results recently obtained utilizing PS matrices from different suppliers, confirms the general validity of the proposed phenomenon.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and additional supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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