In situ electroluminescence color tuning by thermal deprotonation suitable for thermal sensors and anti-fraud labels

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Abstract: A novel and versatile approach to tune photoluminescence and electroluminescence by in situ controlled thermal deprotonation is presented. This methodology, based on a single organic π-conjugated material (pyrene derivative), allows the manufacturing of Organic Light-Emitting Diodes (OLEDs) prototypes by solution methods with controlled tunable emission ranging from the orange (protonated form of the dye) to the blue (pristine or deprotonated form). While several protonation/deprotonation cycles can be performed on thin films, for the devices only one cycle is possible so that their use as anti-fraud labels can be envisaged. OLEDs exhibit daylight visible brightness of 150 cd/m^2 and device lifetime exceeding 30 hours of continuous operation. Thanks to the simplicity of both material design and device fabrication our approach opens new perspectives in the wide field of thermal sensors for customer care or risk perception.

Organic fluorophores are often preferred over their inorganic counterparts in the fields of artificial lighting, display systems and bio-medical tools owing to their low cost, easy color control, solution processability and low toxicity.[1] The tunability of the emissive properties is highly desirable especially in Organic Light-Emitting Diodes (OLEDs) technology,[2] and many different strategies have been employed on this regard. Among those, particularly interesting is the use of single dyes possessing dual emission properties related to different charge transfer characters of their emissive states. Intramolecular proton transfer molecules have been exploited in OLEDs to generate multicolor or white emissions from single molecules,[3],[4],[5] although they are generally susceptible to aggregation quenching processes and to unwanted environmental changes.[5] Organic salts have been used to dope the emissive material in OLEDs, however quenching of the emission by the organic salt occurred at high doping level, giving devices with low performances.[6] Recently thermal-evaporated OLEDs based on a single emitter in both neutral and protonated species have been shown to provide emission from greenish blue to orange by employing different amount of an acid as dopant.[4, 7] To our knowledge, even though highly desirable in view of many advanced applications, the *in situ* color tunability of OLEDs based on a single emitter by an external stimulus has never been reported.[8]

Here we present, for the first time, the *in situ* approach, based on acidochromic and thermal modulation of the properties of a single organic molecule, to tune both photo- (PL) and electroluminescence (EL) on an extremely wide range of colors.

Pyrene and its derivatives have demonstrated to exhibit excellent chromophore features,[9] thanks to their extended π-electron delocalized systems.[10] These fluorophores display blue monomeric and green excimer emission, according to their supramolecular organization,[11] and long lifetime of their excited states. Thanks to these properties, they have been extensively used as sensing materials,[12] for biophysical applications and in OLED technology.[13]

Table 1. PL properties of **1**:PMMA films of different loadings (wt.%) before and after exposure to HCl vapors.

loading	λ_{max}^{PL} (nm)		Shift (eV)	PL QY	
	as-spun	protonated		as-spun	protonated
2%	450	545	0.48	0.69	0.32
5%	490	595	0.45	0.64	0.30
8%	495	596	0.43	0.51	0.18
13%	501	619	0.47	0.45	0.09

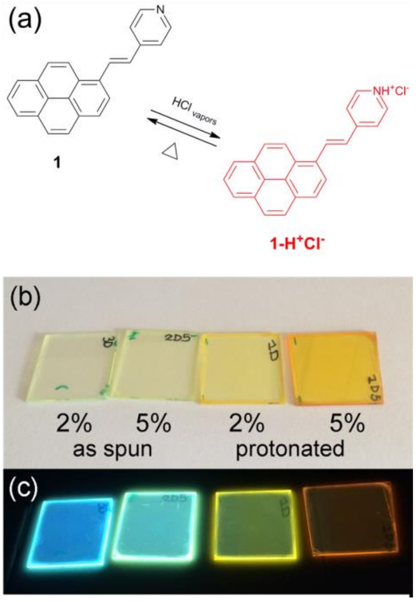

Figure 1. (a) Protonation/deprotonation scheme of **1**; image of spin coated films of **1**:PMMA blends at 2 and 5 wt.% before and after exposure to HCl vapors, under ambient light (b) and UV excitation (c).

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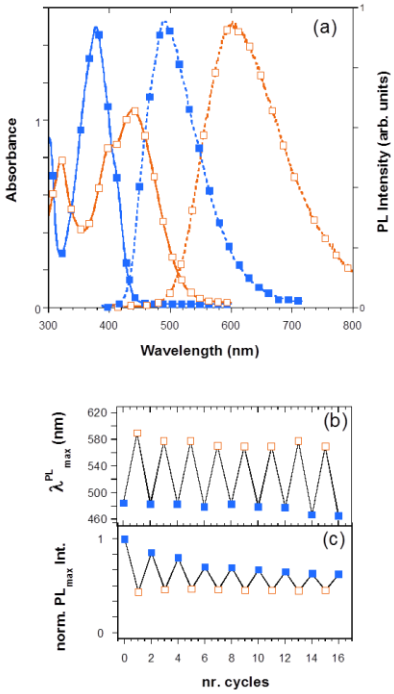

Figure 2. (a) Optical absorption (solid lines) and normalized PL spectra (dotted lines) of the 5 wt.% loading **1**:PMMA film before (■) and after (□) HCl vapors exposure for 90 s. Excitation wavelength is 380 nm. PL peak position (b) and normalized maximum intensity (c) of the as-spun, protonated (■) and thermally deprotonated (110 °C for 600 s) film (□) during several protonation-deprotonation cycles.

We have recently reported the acid-triggered reversible PL and non-linear optical properties of (2-pyrene-1-yl-vinyl)pyridine, hereafter **1**, both in solution and in the solid state upon exposure to HCl and ammonia vapors.[14] The alteration of the linear and nonlinear optical properties of the chromophore is induced by the modulation of its internal charge-transfer due to the external stimulus (Figure 1a and S1). In particular, the solid state interconversion process has been performed on thin films of **1** dispersed in polymethylmethacrylate (PMMA) (2 wt.%) prepared by spin coating.

The protonation procedure is initially applied to **1**:PMMA films of different loadings and the emission properties before and after exposure to HCl vapors are investigated. The emission of the pristine blends red-shifts with increasing dye loading from 2 to 13 %, evidencing a progressive chromophore aggregation that is accompanied by a slight reduction in the PL quantum yield (QY) (Table 1 and Figure S2). By exposure of the films to HCl vapors, a red-shift of about 0.4-0.5 eV in the emission of the blends occurs for all the loadings (Table 1).

Images of spin coated films of **1**:PMMA with 2 wt.% and 5 wt.% loading before and after exposure to HCl vapors are reported in Figure 1b,c. The behavior of the 5 wt.% film is particularly interesting due to the sharp variation in the emission color going from the pristine (blue, peaked at 490 nm) to the protonated (orange, peaked at 595 nm) form (Figure 2a), and, for this reason, we have mainly focused on this loading.

Here the reversibility of the protonation process by thermal treatment is demonstrated. We have determined by PL analysis that the deprotonation (or reconversion) process occurs with

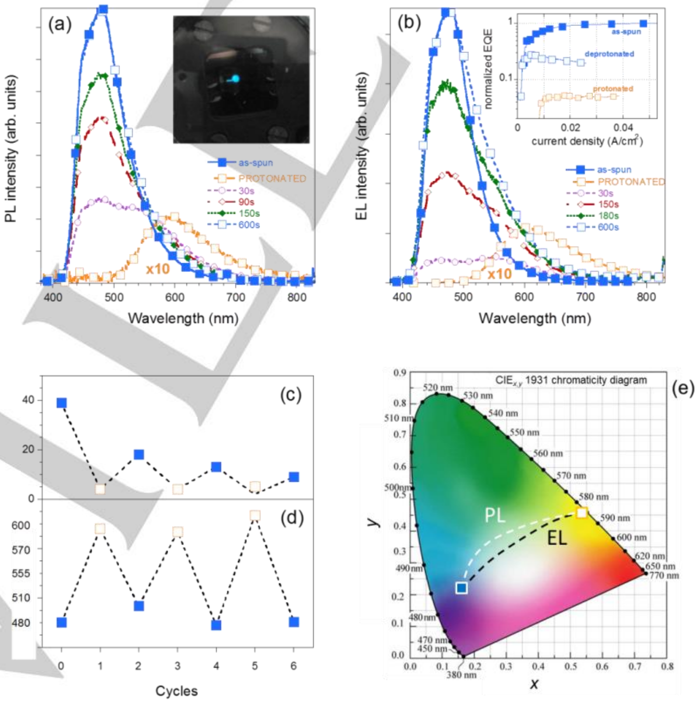

Figure 3. PL (a) and EL (b) spectra of **1**:PVK (5 wt.%) films as-spun (normalized intensity, ■), full protonated (□) and during thermal deprotonation at 110°C. In the inset of (a) working as-spun OLED; In the inset of (b) normalized EQE vs current density for the pristine, protonated and deprotonated device. (c) PL QY and (d) PL peak positions of **1**:PVK (5 wt.%) blends during several protonation (■)/deprotonation (□) cycles (HCl vapor exposure for 90 s and treatment on a heat plate at 110°C for 600 s). (e) Corresponding CIE chromaticity coordinates reporting as-spun (■) and protonated PL/EL (□) together with locus for intermediate treatments.

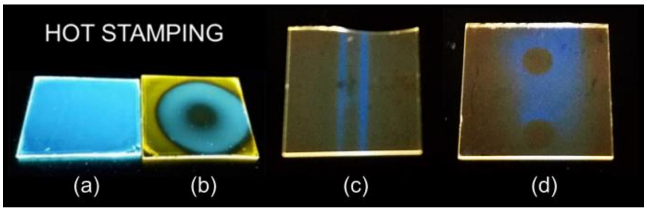

Figure 4. Images, under UV light, of partially protonated/deprotonated films: a) film with 5 wt.% loading **1**:PMMA before (a) and after (b) exposure to HCl vapors followed by partial deprotonation by a heated ring; c) and d) hot stamping of protonated **1**:PVK film with defined shapes.

velocities depending on the temperature. In particular, the full reconversion of a protonated film is achieved in 12 h at 80 °C and in 600 s at 110 °C.

Importantly, several protonation/deprotonation cycles can be performed by alternatively HCl exposure and thermal treatment and the PL emission peak of the pristine film is always recovered (see Figure 2b). Besides, for every reconversion a progressive but slight reduction of the PL QY of the deprotonated form is observed (Figure 2c).

The process is not only fully reversible, but also intermediate steps can be reached (see Figure 3) so that the entire visible range of emissions can be covered in a finely controlled way during the thermal treatment.

Due to the insulating properties of PMMA, in view of device applicability, we have optically characterized blends of **1** in polyvinylcarbazole (PVK) which possesses optimal charge transport properties and is widely used as host for OLEDs active layers.[15]

The protonation/deprotonation protocol developed for PMMA is applied to **1**:PVK 5 wt.% blend films. The optical behavior is fully consistent with that observed for **1**:PMMA. PL emission of **1**:PVK films shifts from blue (pristine) to orange (by HCl exposure) and back to blue upon thermal treatment (Figure 3a). A slight reduction of PL QY is observed, as in PMMA, along with cycle repetitions (Fig. 3c,d).

We have manufactured OLEDs based on 5 wt.% **1**:PVK film as active layer to investigate the electro-optical behavior upon protonation and deprotonation of the dye.

The control as-spun device is fabricated by spin coating in air the **1**:PVK CH_2Cl_2 solution over an ITO covered glass with a thin layer of PEDOT:PSS and successively capped by Ba/Al electrode to achieve the architecture ITO/PEDOT:PSS/**1**:PVK/Ba/Al. Furthermore, a bi-layer OLED which embeds an interfacial polymer layer (electron injecting polymer, or EIL) to control electron injection and exciton confinement is built up. The insertion of EIL is an established approach to achieve efficient and stable devices. The polar polymer poly[(2,7-(9,9′-dioctyl)fluorene)-alt-(2,7-(9,9′-bis(5″-trimethylammonium bromide)pentyl)-fluorene)] (Figure S6) is employed as EIL.[16] The multilayer blue emitting devices exhibit performances in air that well fulfill the requirements of application as smart label. In fact, besides a modest external quantum efficiency (EQE), which is not an issue at proof-of-concept stage, a good brightness above 150 cd/m^2, CIE chromaticity coordinates (0.16; 0.22) and good operational stability, (retaining over 50% of the brightness for over 30 hours of continuous operation at 10 mA/cm^2) are observed.

To easier demonstrate *in situ* tunabilty we have used the single layer architecture protocol: the uncomplete device ITO/PEDOT:PSS/**1**:PVK is exposed to HCl vapors for 90 s monitoring the protonation reaction by PL analysis. Successively, the Ba/Al cathode is deposited in an high vacuum chamber to finalize the prototype. The OLED at full protonation switches on at about 15-18 V and emits orange light. Thereafter, it is thermally reconverted to pristine form (600 s at 110 °C) and the intermediate EL spectra are registered (Figure 3b).

The spectral changes during thermal deprotonation cover a large portion of the visible range thus allowing to easily tune the OLED emission color from orange (0.54, 0.45) to blue (0.16, 0.22), passing through white (0.31, 0.36) (see CIE diagram in Figure 3e).

According to what has been observed for the PL QY of **1**:PVK films, the EQE of the OLED is reduced upon protonation (inset of Figure 3b and Figure 3c) with respect to the as-spun one. During the reconversion process, EQE partially recovers the value of the pristine device.

To our knowledge, this is the first time that the EL color modulation is accomplished by *in situ* thermal deprotonation of the dye. This strategy opens to smart applications making challenging to realize small, cheap and integrated devices for on demand tunable-color light sources or stimuli responsive labels.[17]

It should be underlined that, contrarily to PL reversibility of the films, after thermal deprotonation the OLED prototypes cannot be protonated again, since acid exposure irreversibly damages the metallic cathode (Figure S8) making the devices disposable. Any thermal stress (both long time exposure to mild temperatures or short time exposure to higher temperatures) will then result in the irreversible change of the OLED emission color from orange to blue. This feature offers unique and promising advantages for specific applications such as anti-fraud smart labels which retain the thermal history (*i.e.* sterilization) of a packaged product and can be proposed as pre-purchasing information for the consumers.

Another aspect of the versatility of the method is the possibility to obtain dual color emission by selectively heating the film, *i.e.* by writing on the film with a heating pen or by applying a heated stamp for few seconds, as shown in Figure 4.

In this view, a simple multi-color proof-of-concept prototype with a selective local protonation/deprotonation of the active layer is manufactured (Figure 5). Half of the protonated active layer is reconverted by heating at 110 °C for 600 s on a hot plate and afterwards the cathode is deposited through a patterned mask to form 6 squared pixels (area 2.5 mm x 2.5 mm).

Three neighboring representative pixels of the same device are switched on individually and emit blue, white and orange light respectively (Figure 5f-h). The border area between protonated and reconverted part of the film is broad and generates white emission as combination between blue and orange. The orange pixel will switch to white and then to blue upon heating the devices on a timescale which, as shown, depends on the temperature. By simply switching on the three adjacent pixels and comparing their color, instant information of the amount of heat absorbed by the label can be achieved.

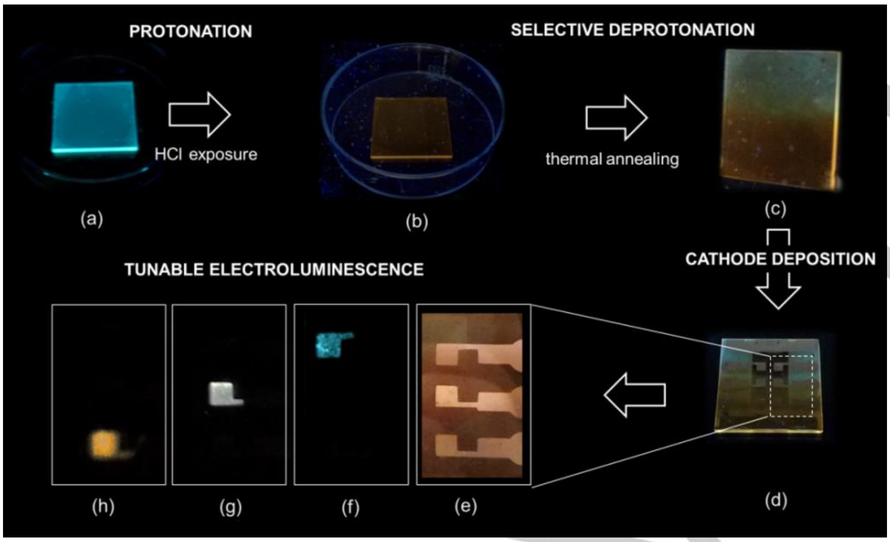

Figure 5. Manufacturing of tunable-color OLED by selective local protonation/deprotonation of the active layer. (a) as-spun **1**:PVK (5 wt.%) film; (b) film after exposure to HCl vapors for 90 s; (c) film after partial deprotonation; (d) patterned Ba/Al cathode; all the images are captured by exciting film with UV light. (e) devices in the off state positioned into testing chamber; (f) deprotonated pixel emitting in blue light; (g) partially protonated/deprotonated pixel emitting white light; (h) full protonated pixel with orange electroluminescence. The pixels are switched on selectively by applying voltage in the range 15-25 V.

Used as sensor to monitor the thermal history of a product, the fluorescent films or electroluminescent labels provide two ways to convey the information for customer care.

In conclusion, multi-color photoluminescence (PL) and electroluminescence (EL) have been achieved based on a single fluorophore by *in situ* controlled thermal deprotonation. These unique properties can be exploited to fabricate both fluorescent and electroluminescent smart labels for food packaging that preserve the information on their thermal history (for example sterilization of canned products), opening to new perspectives in the application of OLEDs for customer care or risk perception. A good brightness (above 150 cd/m^2) and operational stability (more than 30 hours), combined to the irreversibility of the deprotonation in OLEDs, well fulfil the requirements to manufacture stimuli-responsive anti-fraud labels. In addition, this novel and simple approach has potential applicability in fabricating multi-color or white OLEDs considering the easiness and low costs of both material design and device fabrication.

Experimental Section

All reagents and solvents were purchased from Sigma Aldrich.

Compound **1** was prepared following a published procedure.[14] Thin films of **1** dispersed in polymethylmethacrylate (PMMA) were prepared by spin coating few drops of a dichloromethane solution (**1**:PMMA = 2, 5, 8 or 13 wt%; PMMA = 10 wt% with respect to the solvent) on a glass or quartz substrates. UV-Vis absorption spectra were obtained with a Perkin Elmer Lambda 900 spectrometer and photoluminescence (PL) spectra with modified NanoLog-TCSPC by Horiba. Spectra were corrected for the instrument response. PL quantum yields (PL QYs) of the films were obtained by using a home-made integrating sphere, as previously reported.[18] The solution of emitting blend **1**:PVK 5wt%, 15 mg/ml in $CHCl_3$, was deposited on device substrates by spin-coating technique. The manufacture of the devices followed the procedure reported elsewhere.[15]

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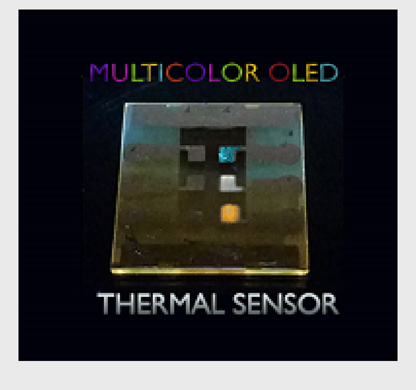

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