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COMMUNICATION

## Protonable Pyrimidine Derivative for White Light Emission

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**White photoluminescence both in solution and the solid-state was obtained by the controlled protonation of a blue emitting 4,6-bis(arylvinyl)pyrimidine, which resulted in the formation of an orange emissive acidified form. This dye has potential applications in the fabrication of white OLEDs based on only one material.**

In the context of the reduction of energy consumption, and taking into account that lighting accounts for ~20% of energy consumption worldwide, there is great interest in research into new light emitting devices, particularly Light Emitting Diodes (LED), that consume less energy.<sup>1</sup>

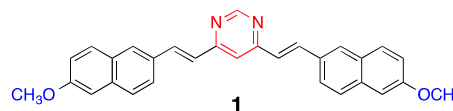
In the field of light-emitting molecules, organic materials that incorporate a  $\pi$ -conjugated backbone are generally preferred over their inorganic counterparts owing to their low cost, ease of fine-tuning, solution processability, low toxicity and sufficient flexibility for device fabrication.<sup>2</sup>

Organic LEDs (OLEDs) that emit white light were first reported by Kido et al.<sup>3</sup> White OLEDs (WOLEDs) can now outperform incandescent light bulbs and even fluorescent tubes in terms of luminous efficiency.<sup>4</sup> A good white-light emitter should be a 'warm' white, as defined by colour coordinates close to the Planckian locus around the equi-energy white point ( $x = 0.33$ ,  $y = 0.33$  in the Commission International de l'Eclairage (CIE) 1931 diagram).<sup>2d,5</sup>

Various methods for the fabrication of WOLEDs have been reported. Such devices are generally obtained by doping mixed emitting molecules of complementary colours either in a single emitting layer<sup>6</sup> or in multi-emitting layers.<sup>7</sup> Unfortunately, this strategy generally requires a complex and costly fabrication process. A new strategy for WOLED fabrication has recently been proposed and this involves the use of only one emitting material

that can take two forms of complementary emitting colours. Some examples have been described in the literature and these consist of monomer/excimer,<sup>8</sup> neutral/protonated,<sup>9</sup> neutral/deprotonated species,<sup>10</sup> or free/complexed ligand.<sup>11</sup>

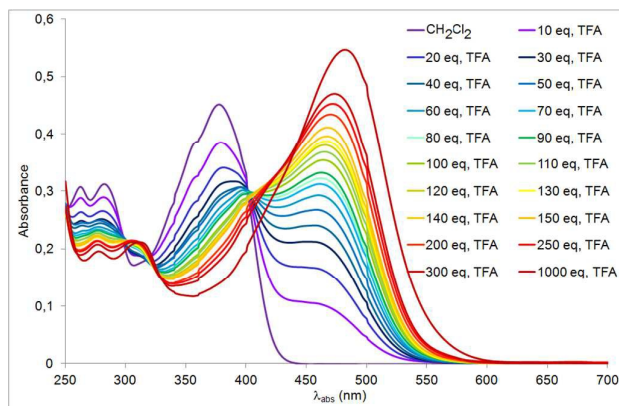
The replacement of CH groups by N atoms in  $\pi$ -conjugated frameworks dramatically changes the positions of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and the emission spectra.<sup>12</sup> In this context, we have described a large library of push-pull pyrimidine chromophores.<sup>13</sup> When substituted by electron-donating fragments via  $\pi$ -conjugated linkers, these compounds are highly fluorescent and their emission properties are highly sensitive to external stimuli such as solvent polarity,<sup>13,14</sup> pH,<sup>13b-e,14a</sup> and metal cation complexation.<sup>15</sup> Protonation of push-pull pyrimidine derivatives leads to a bathochromic shift in the absorption. Whereas the emission is often quenched upon protonation, methoxy-substituted pyrimidines generally exhibit a red-shifted emission.<sup>16</sup> However, it should be noted that methoxy-substituted compounds with high emission quantum yields require an extended  $\pi$ -conjugated bridge.<sup>17</sup> We recently described the synthesis and basic photophysical properties of 4,6-bis[2-(6-methoxynaphthalen-2-yl)-vinyl]pyrimidine **1** (Chart 1). The synthesis of **1** is straightforward, affordable and environmentally friendly. In solution of dichloromethane this compound emits blue light at 470 nm ( $\Phi_F = 0.38$ ) that can be tuned to orange by protonation.<sup>13e</sup> Herein, we describe the emission properties of a mixture of neutral and protonated forms of compound **1** both in solution and in thin films. The controlled protonation of this blue emitting dye led to white photoluminescence. The electronic properties were also studied by cyclic voltammetry.

Chart 1. Structure of compound **1**.

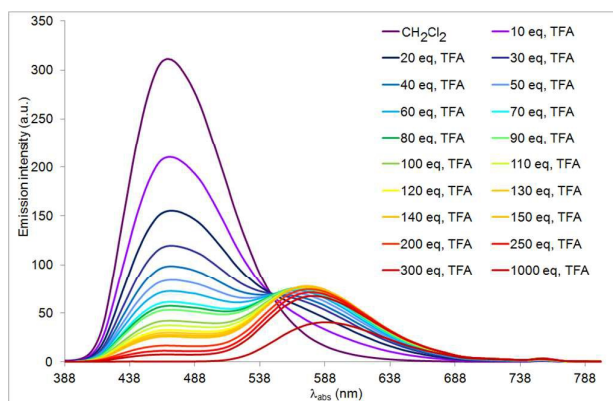
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<sup>b</sup> Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain. E-mail: [julian.rodriquez@uclm.es](mailto:julian.rodriquez@uclm.es) Tel + 34 926 295 300 Electronic Supplementary Information (ESI) available: <sup>1</sup>H and <sup>13</sup>C nmr spectra of **1** before and after protonation, influence of excitation wavelength on emission spectrum of **1** with 100 eq of TFA, differential pulse voltammetry and TGA plot. See DOI: 10.1039/x0xx00000x

The changes in the UV-vis spectra of **1** upon addition of trifluoroacetic acid (TFA) are illustrated in Figure 1. The spectra show the progressive attenuation of the charge transfer absorption band for the neutral compound on increasing the concentration of acid, whereas a new red-shifted band corresponding to the protonated species appeared. This bathochromic shift is explained by an enhancement of the intramolecular charge transfer (ICT) into the molecule due to the increase in the electron-attracting character of the pyrimidine ring by protonation. As far as the photoluminescence is concerned, the same trend was observed: addition of TFA led to a decrease in the emission band intensity and a new red-shifted band appeared (Figure 2).

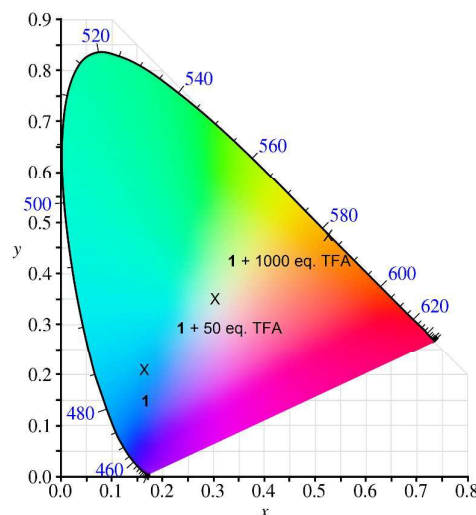


**Figure 1:** Changes in the absorption spectra of **1** ( $c = 8.8 \cdot 10^{-3}$  M) in  $\text{CH}_2\text{Cl}_2$  upon addition of TFA (20 to 1000 equivalents).



**Figure 2:** Changes in the emission spectra of **1** ( $c = 8.8 \cdot 10^{-3}$  M) in  $\text{CH}_2\text{Cl}_2$  upon addition of TFA (20 to 1000 equivalents),  $\lambda_{\text{exc}} = 377$  nm.

When excited at 377 nm, the intensity of both bands became similar after the addition of 50–100 equivalents of TFA. With 50 equivalents of TFA, the CIE coordinates (0.30, 0.35) were very close to those of pure white light emission (0.33, 0.33) (Figure 3). This solution showed an intense white colour under UV irradiation, whereas solutions of non-protonated and fully-protonated compound **1** appeared blue and orange, respectively (Figure 4). It is worth noting that changes in the excitation wavelength also dramatically modified the relative intensities of both bands (see ESI, Figure S1).



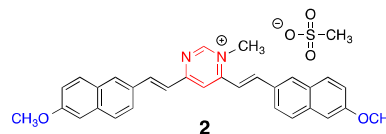
**Figure 3:** Chromaticity of the fluorescence colour of **1** in  $\text{CH}_2\text{Cl}_2$  obtained in the absence and the presence of TFA in a 1931 CIE diagram.



**Figure 4:** Changes in the colour of a  $\text{CH}_2\text{Cl}_2$  solution of **1** ( $c = 2.2 \cdot 10^{-4}$  M, left) after the addition of 50 equivalents (middle) and 1000 equivalents of TFA (right). Photographs were taken in the dark upon irradiation with a hand-held UV lamp ( $\lambda_{\text{em}} = 366$  nm).

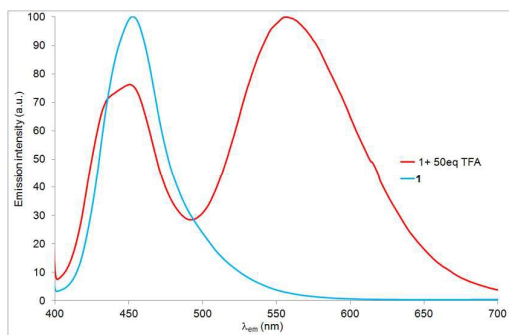
The large excess of acid required to see the change in the UV-vis and emission spectra is in line with the reduced basicity of the nitrogen atoms of the pyrimidine ring. Solvents such as diethyl ether and ethanol are basic enough to revert the process. In both the absorption and emission spectra, isobestic points were observed for low concentrations of acid. Nevertheless, these isobestic points disappeared due to the significant change in polarity when the concentration of acid increased. It should also be noted that above 200 equivalents of TFA, the intensity of the red-shifted band began to decrease for the same reason.

Protonation was also accompanied by a noticeable downfield shift of most of the signals in the  $^1\text{H}$  NMR spectrum of chromophore **1** (see ESI, Figure S2). In order to confirm that protonation took place on the pyrimidine ring, we prepared the methylated species **2** (Chart 2) that showed similar absorption and emission spectra to those of the protonated form of **1**, supporting the protonation of the pyrimidine ring in the presence of TFA. (see ESI and Figures S3 and S4).



**Chart 2.** Methylated species **2**.

Despite their high emission efficiency in solution, many organic materials are non-luminescent in the solid state because of the fluorescence quenching caused by intermolecular interactions occurring in the condensed phase. Thin films formed by spray deposition of a  $\text{CH}_2\text{Cl}_2$  solution of **1** were luminescent but the emission spectra were significantly modified, a finding that suggests the formation of aggregates. One way to overcome this type of problem involves the incorporation of the fluorophore into a polymer matrix;<sup>18</sup> polystyrene is particularly adapted in this context.<sup>19</sup> Thus, thin films of polystyrene doped with 1 wt% of **1** were obtained by spray deposition on glass substrates. These films exhibited a slightly blue-shifted emission ( $\lambda_{\text{em}} = 443 \text{ nm}$ ,  $\Phi_{\text{F}} = 0.34$ ) when compared with chromophore **1** in solution ( $\lambda_{\text{em}} = 470 \text{ nm}$ ). Once again, the addition of 50 equivalents of TFA in the solution used for spray deposition resulted in a film that showed two emission bands ( $\Phi_{\text{F}} = 0.33$ ) with CIE coordinates of (0.31, 0.30), i.e., close to pure white (Figure 5). The change in the emission colour could easily be seen with the naked eye, as shown in Figure 6. In contrast to the solution, the thin film of the fully protonated compound was only weakly luminescent.



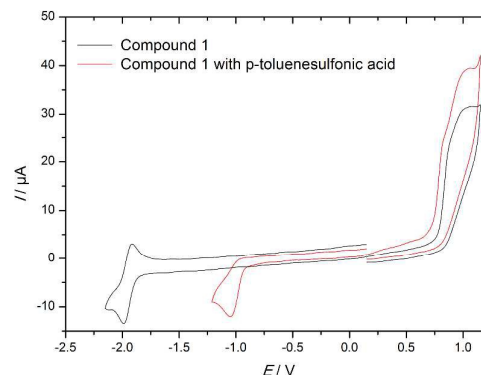
**Figure 5:** Emission spectra of a polystyrene thin film doped with 1 wt% of **1** in the absence (blue) and the presence (red, 50 equivalents) of TFA.



**Figure 6:** Colours of polystyrene thin films doped with **1** (1 wt%) in the absence (left) and the presence of 50 equivalents (middle) and 1000 equivalents (right) of TFA. Photographs were taken in the dark upon irradiation with a hand-held UV lamp ( $\lambda_{\text{em}} = 366 \text{ nm}$ ).

In an effort to gain further insights into the electronic properties of compound **1** and its protonated form, the redox properties were measured by cyclic voltammetry, in DMF- $[\text{Bu}_4\text{N}][\text{PF}_6]$ , in the absence and presence of *p*-toluenesulfonic acid (*p*-TsOH). Compound **1** showed an irreversible oxidation peak and a reversible one-electron reduction at  $E_{1/2} = -1.95 \text{ V}$  vs the ferrocenium/ferrocene couple ( $\text{Fc}^{+/0}$ ) (Figure 7). The oxidation peak was followed by a close irreversible process, which precluded the accurate determination of the oxidation potential. Nevertheless, on using differential pulse voltammetry it was possible to determine the potential of this peak as  $E_{\text{p}}^{\text{ox}} = 0.82 \text{ V}$  vs  $\text{Fc}^{+/0}$  (see ESI, Figure S5). The addition of *p*-TsOH led to a new irreversible reduction peak

at  $E_{\text{p}}^{\text{red}} = -1.05 \text{ V}$  vs  $\text{Fc}^{+/0}$ , a potential that is less negative than the one for the reduction of **1** (Table 1). Although the shift in the reduction peak was noteworthy (0.90 V), a significant effect was not observed in the oxidation process (0.03 V).



**Figure 7:** Cyclic voltammogram of **1** ( $c = 1.5 \text{ mM}$ ) before (black) and after (red) addition of *p*-TsOH.  $E$  (V) vs  $\text{Fc}^{+/0}$  couple. Scan rate  $\nu = 0.1 \text{ V s}^{-1}$ .

**Table 1:** Cyclic voltammetry data for compound **1**.  $E$  (V) vs ferrocene.

Compound	$E_{\text{p}}^{\text{ox}}$ (V)	$E_{1/2}^{\text{red}}$ (V)
<b>1</b>	0.82 <sup>a</sup>	-1.95
<b>1</b> + $\text{H}^+$	0.79 <sup>a</sup>	-1.05 <sup>b</sup>

<sup>a</sup> The value could not be determined accurately by cyclic voltammetry and it was measured by differential pulse voltammetry. <sup>b</sup> Irreversible peak, the value stands for  $E_{\text{p}}$ .

Thermal stability is a key parameter for OLED applications. Thermogravimetric analysis (TGA) of **1** (see ESI, Figure S6) showed good stability with a thermal decomposition occurring at around  $400 \text{ }^\circ\text{C}$ , which is sufficiently high for applications in electro-optical device preparation.

In summary, a pyrimidine chromophore that exhibited white photoluminescence by controlled protonation both in solution and the solid state has been designed. The white luminescence is based on the partial protonation of this blue-light emitting dye. Protonation of the electron-deficient pyrimidine ring provides a significant enhancement of its electron-withdrawing character, as shown by the dramatic effect on the reduction potential, and leads to a red-shifted luminescence. The electroluminescence properties of this chromophore are currently under investigation.

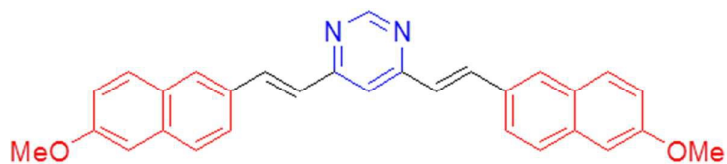
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The protonation of a blue emitting pyrimidine chromophore resulted in the formation of an orange emissive acidified form. In adequate proportion of neutral and protonated forms, the emission of white light is observed either in solution or in polystyrene thin film.



Neutral form

$\lambda_{em} = 470 \text{ nm}$

$\Phi_F = 0.37$

Protonated form

$\lambda_{em} = 590 \text{ nm}$

$\Phi_F = 0.19$

