

## Protonable nitrogen-based heterocyclic chromophores for white light emission.

<sup>1</sup> Sylvain Achelle, <sup>2</sup> Julián Rodríguez-López and <sup>1</sup>Françoise Robin-le Guen.

<sup>1</sup> Univ Rennes, CNRS, Institut des Sciences Chimiques de Rennes, UMR 6226, F 35000 Rennes, France <sup>2</sup> Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, 13071 Ciudad Real,

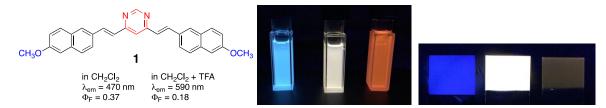
Spain.

In the context of the reduction of energy consumption, and taking into account that lighting accounts for ~20% of energy consumption worldwide, there is a great interest in research into new light emitting devices, particularly Light Emitting Diodes (LED), that consume less energy. White Organic LEDs (WOLEDs), first reported by Kido,<sup>1</sup> can now outperform incandescent light bulbs and even fluorescent tubes in terms of luminous efficiency. 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 Internationale de l'Eclairage* (CIE) 1931 diagram).<sup>2</sup>

A new strategy for WOLED fabrication has recently emerged that involves the use of only one emitting material with two forms of complementary colours, such as neutral/protonated species.<sup>3</sup>

During the past decade, we have described a large library of push-pull diazine chromophores.<sup>4</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, pH, and metal cation complexation. 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>5</sup> However, it should be noted that methoxy-substituted compounds with high emission quantum yields require an extended  $\pi$ -conjugated bridge.<sup>6</sup> Some compounds of our library possess these requested specifications.<sup>7</sup> Recently we have extended this strategy to pyridine derivatives.<sup>8</sup>

In this communication, we will describe the emission properties of a mixture of neutral and protonated forms of these compounds both in solution and in thin films. The controlled protonation of these blue emitting dyes led to white photoluminescence (Figure 1).



**Figure 1**. Chemical structure of **1** (left). Colours of  $CH_2Cl_2$  solutions of **1** (middle) and polystyrene thin films doped with 1 wt% of **1** (right) in absence and the presence of 50 and 1000 equivalents of trifluoroacetic acid.

## **Bibliography**

<sup>1</sup> J. Kido et al Appl. Phys. Lett. **1994**, 64, 815.

<sup>2</sup> S. Mukherjee et al. Dyes Pigm. 2014, 110, 2.

<sup>3</sup> D. Liu *et al. Chem Commun.* **2013**, *49*, 10001.

<sup>4</sup> a) S. Achelle *et al. J. Org. Chem.* **2009**, *74*, 3711. b) C. Hadad *et al. J. Org. Chem.* **2011**, *76*, 3837. c) S. Achelle *et al. J. Org. Chem.* **2014**, *79*, 7564. d) S. Achelle *et al. RSC Adv.* **2015**, *5*, 39218. e) K. Hoffert *et al. Eur. J. Org. Chem.* **2017**, 523.

- <sup>5</sup> S. Achelle *et al. Tetrahedron Lett.* **2013**, *54*, 4491.
- <sup>6</sup> C. Denneval et al. Dyes Pigm. 2014, 110, 49.
- <sup>7</sup> a) S. Achelle et al. RSC Adv. 2015, 5, 107396. b) S. Achelle et al. J. Phys. Chem. C 2016, 120, 26986.
- <sup>8</sup> J. Tydlitát *et al. Dyes Pigm.* **2017**, *146*, 467.