Benzothiadiazole-based luminescent stimuli-responsive materials: The role of "2S–2N" square synthon on their supramolecular arrangement and switchable behaviour

B. Gómez-Lor, M. Echeverri

Instituto de Ciencia de Materiales de Madrid, CSIC Cantoblanco, 28049 Madrid (Spain).

bgl@icmm.csic.es

Materials which switch their optical spectroscopic properties (*i.e.*, color, fluorescence) upon physical external stimulation (*i.e.*, pressure, temperature) arouse much interest owing to their potential applications in fields as varied as sensing, construction, recording, display technologies or rewritable paper [1]. In the quest for new organic stimuli responsive materials, the 2,1,3-benzothiadiazole moiety (BTD) have emerged as a promising building block, since the absorption and emission properties of this moiety is strongly influenced by its external environment. In the last few years several BTD-based chromogenic and fluorogenic materials have been reported, but although there are some recent exceptions, in most examples crystalline-to-amorphous transitions are in the origin of this behaviour. This fact prevents an in-depth study of the mechanism behind this process and limits the rational development of new chromophores with predesigned properties.

Herein we present a variety of BTD-derivatives, which crystallizes in different polymorphs with layer-like organization, exhibit distinct light emitting properties under UV illumination and can be readily interconverted by means of external stimuli [2, 3]. Through a joined crystallographic, spectroscopical and theoretical approach we have been able to unravel the origin of the polymorphic transformation and fluorogenic behavior.

In this communication we will discuss interesting design principles, to obtain novel BTD stimuli-responsive organic materials that we have been able to establish as a result of this study. A special emphasis will be placed on the role of "2S–2N" square synthon [4] in the supramolecular arrangement and switchable light emission properties of BTD derivatives.

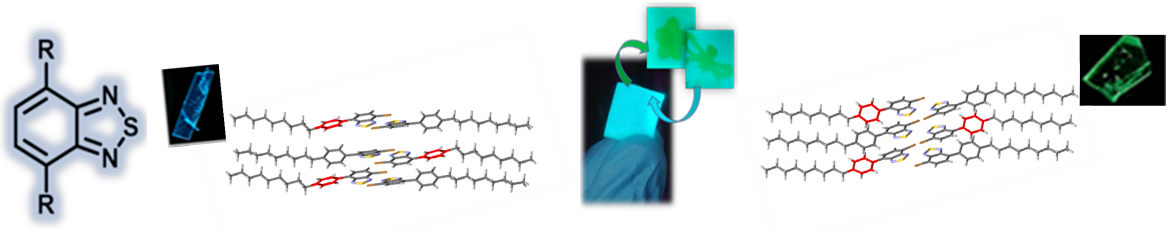

Figure 1. Example of one of the BTD -based mechanochromic systems developed.

[1] Roy, B.; Reddy, M. C.; Hazra, P. (2018) *Chem. Sci.* **9,** 3592

[2] Echeverri, M.; Ruiz, C.; Gámez-Valenzuela, S.; Martín, I.; Delgado, M. C. R.; Gutiérrez-Puebla, E.; Monge, M. Á.; Aguirre-Díaz, L. M. & Gómez-Lor, B. (2020) *J. Am. Chem. Soc.* **142**, 17147.

[3] Echeverri, M.; Ruiz, C.; Gámez-Valenzuela, S.; Alonso-Navarro, M.; Gutierrez-Puebla, E.; Serrano, J. L.; Ruiz Delgado, M. C. & Gómez-Lor, B. (2020) *ACS Appl. Mater. Interfaces* **12**, 10929.

[4] Ams, M. R.; Trapp, N.; Schwab, A.; Milić, J. V.; Diederich, F. (2019) *Chem. A Eur. J* **25**, 323.

Keywords: mechanochromism, thermocromism, "2S–2N" square synthon.