

Thermally switchable upconversion emission

Roscini Claudio¹, Hernando Jordi², Ruiz-Molina Daniel¹, Massaro Giuseppina³,
Latterini Loredana³

¹ *Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, 08193 Barcelona, Spain*

² *Departament de Química, Universitat Autònoma de Barcelona, Edifici C/n, Campus UAB, 08193 Cerdanyola del Vallès, Spain*

³ *Department of Chemistry, Biology and Biotechnology, Perugia University, Via Elce di sotto, 8, 06123 Perugia, Italy*

E-mail: claudio.roschini@icn2.cat

Photon upconversion (UC), the generation of high-energy luminescence by sequential absorption of two or more photons of lower energy,^[1,2] has gained much attention in recent years for its potential applicability in NIR absorbing photovoltaic cells^[3] and biological fluorescent markers.^[4] More recently, switchable luminescence based on upconversion has been proposed for temporal and spatial high-resolution fluorescence microscopy^[5] and multicolor barcoding.^[6] So far the reported strategies to achieve this goal, either based on rare-earth nanoparticles or triplet-triplet annihilation (TTA) of organic dyes, involve complex molecular design or particles synthesis, tight optical conditions, high power density irradiations and/or the use of auxiliary external components to induce luminescence switching. Herein we report a counterintuitive but straightforward and universal approach to obtain temperature-responsive switchable TTA upconversion emission.^[7] This strategy, based on low-concentrated solutions of the molecular material (the sensitizer and the emitter) in aliphatic phase-changing media (PCM), involves the reversible aggregation of the molecular material, through a temperature induced phase change. With this strategy, sharp, reversible and nearly complete interconversion between high-energy emitter upconverted fluorescence and low-energy sensitizer luminescence was achieved around the melting point of PCMs (Figure 1).

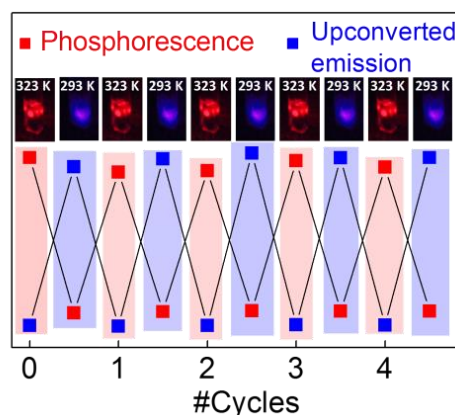


Figure 1. Thermally induced switchable UC/phosphorescence emission

Moreover, by simply changing the dyes pair or the PCM we were able to tune the spectral response and the switching temperature on command. Noticeably, when using PCMs with melting points above the room temperature, TTA-UC emission from a solid material with low dye concentration was achieved.

Funding: Ministero Istruzione dell'Università e della Ricerca (MIUR) through the program "Fondo Giovani XXVIII Ciclo ambito 3", Spanish government and FEDER funds with projects MAT2012-38318-C03-02 and CTQ2012-30853, Severo Ochoa Program with Grant SEV-2013-0295

References:

- [1] J. Zhou, Q. Liu, W. Feng, Y. Sun, F. Li, *Chem. Rev.*, **2015**, 115, 395
- [2] N. Yanai, N. Kimizuka, *Chem Commun*, **2016**, 52, 5354
- [3] Y. Y. Cheng, B. Fückel, R. W. MacQueen, T. Khoury, R. G. C. R. Clady, T. F. Schulze, N. J. Ekins-Daukes, M. J. Crossley, B. Stannowski, K. Lips, T. W. Schmidt, *Energy Environ. Sci.* **2012**, 5, 6953
- [4] Q. Liu, T. Yang, W. Feng, F. Li, *J. Am. Chem. Soc.* **2012**, 134, 5390
- [5] M. K. Lee, P. Rai, J. Williams, R. J. Twieg, W. E. Moerner, *J. Am. Chem. Soc.* **2014**, 136, 14003
- [6] F. Zhang, Q. Shi,; Y. Zhang, Y. Shi, K. Ding, D. Zhao, D. G. Stucky, *Adv. Mater.* **2011**, 23, 3775
- [7] G. Massaro, J. Hernando, D. Ruiz-Molina, C. Roscini, L. Latterini, *Chem. Mater.* **2016**, 28, 738