Piezochromic properties of a D-A-D platform: A joint experimental and theoretical perspective

S. Fernández-Palacios [a] M. Peña-Álvarez [b], Y. Takeda [c], S. Minakata [c], M. Moreno Oliva [a] and M.C. Ruiz Delgado [a].

[a] *Department of Physical Chemistry, University of Malaga, Boulevard Louis Pasteur Campus Teatinos, 29071, Spain.*

[b] *School of Physics and Astronomy and Centre for Science at Extreme Conditions, University of Edinburgh, EH9 3FD Edinburgh, United Kingdom*

[c] *Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871, Japan*

e-mail: sarafpc@uma.es

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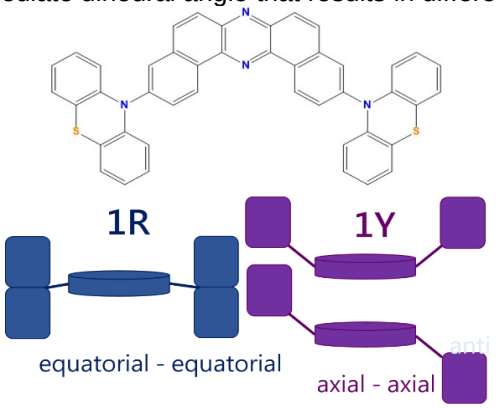
Organic π-conjugated molecules with mechanochromic luminescence properties have attracted great interest in the last two decades due to their numerous applications in the optoelectronic field, such as sensors, probes and security inks. Materials that modify their colour under pressure are known as piezochromic materials. Usually, this variation is provoked by changes in the molecular structure, for example, crystal-to-amorphous phase transitions, modifications in dihedral angles or bond distances, and intermolecular interactions. The molecule proposed in this study is a TADF (Thermally activated delayed fluorescence) U-shaped molecule composed by two donors and one acceptor (D-A-D) units with a π-conjugated skeleton [1]. It was synthetized as a powder which under different crystallization methods gives rise to different conformers varying the dihedral angle of the bond that links the D and A units. The donors are two phenothiazine units and the acceptor is a dibenzo[a,j]phenazine unit located in the central core. Two different conformers have been analysed: the quasi equatorial - quasi equatorial (denoted as 1R) and the quasi axial - quasi axial (denoted as 1Y). In this project, we study the configurational changes triggering the piezochromic effects combining density functional theory (DFT) calculations with Raman spectroscopy experiments of the 1R and 1Y conformers during heating or in compression via a sapphire anvil cell [2]. Both show pressure and temperature dependence properties. Besides, these changes are reversible meaning that when the stimuli stop they revert to its original conformation. When these molecules are exposed to different ambient (like pressure or temperature variations) they evolved to a third conformer with an intermediate dihedral angle that results in different Raman, emission and absorption behaviour.

a)



b)

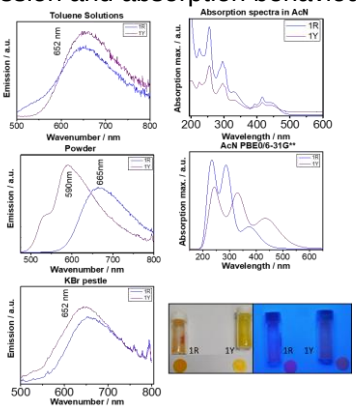


Figure: (a) Molecular structures of both conformers (left). (b) Fluorescence emission and UV-Vis absorption spectra of 1R and 1Y conformers in solution (top), as powder (midle) or KBr pellets (bottom).

References

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