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Crystal structure dependent luminescence of a polyaromatic compound

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Nowadays groups are synthetizing polyaromatic molecules in order to obtain stable and luminescent organic compounds with potential use as active layers in OLEDs. In addition to molecular structure, scientists must have in mind the supramolecular structures of optically active materials might play an important role in the emissions, such as when the excited-state intramolecular protonic transfer (ESIPT) can participate. For ESIPT to occur the correct atomic orientation is required, and, thus, in solid state many other variables act to modulate the emission. One can point the presence of polar crystallization molecules competing for the intramolecular hydrogen-bonds, occurrence of polymorphs, etc. Having all of this in mind we prepared the fluorescent polyaromatic 6′,7′-bis(*N*-tosylamide)-quinoxaline-[2′,3′-d]-1,10-phenanthrene (FTNH), a compound presenting ESIPT. Here we report its crystal structure dependent luminescence obtained from two different solvates and one polymorph at high pressure.

1α, the FTNH synthesized and crystallized from methanolic solution is a yellow crystalline material that brights light green under 365 nm UV-light (Fig 1a). It presents an intramolecular NH···N interaction, which indicates a possible intramolecular proton transfer and thus the emission is predominantly caused by ESIPT. **2** is the dmso-solvate FTNH·dmso, recrystallized in this same solvent. The crystallization molecule acts binding both NH groups to it, via intermolecular hydrogen bonds (Fig 1b). That means the yellow needles bright aqua green as consequence of more energy loss due to extra stabilization of ESIPT excited state in presence of the solvent.[1] **1β** is a non-crystalline polymorph obtained by crushing **1α**. The solid changes its color from yellow-orange to a reddish-orange in the process and under UV-light it brights pink. The Fig 1c shows the powder diffraction before and after crushing it, where only the **1α** phase peaks is observed, meaning the conversion is partial and **1β** has low crystallinity or is non-crystalline. The solid-state spectra (Fig 1d) of **1α** presents a maximum at 468 nm, for **2** at 490 nm and for **1β** two maxima is observed, one at 468 and 625 nm. The pink emission for **1β** is then caused by the combination of residual **1α** and the new phase emissions.

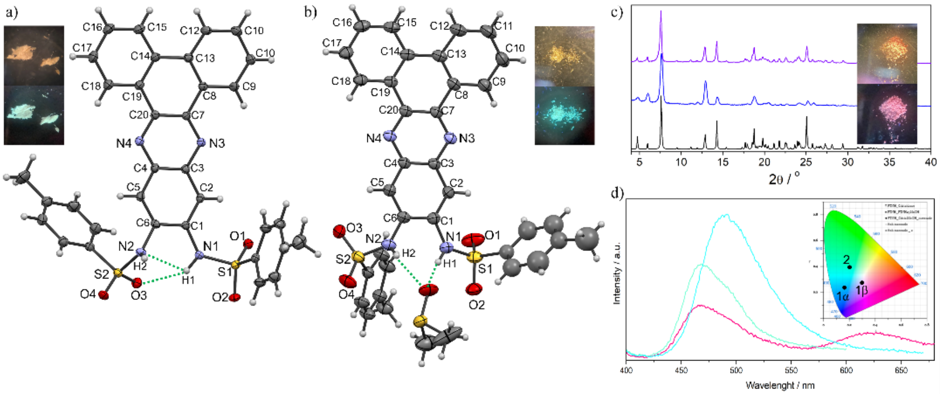

Fig 1 – Crystal struture of (a) 1α and (b) 2 with an image of crystals under white and UV-ligh. (c) Calculated X-ray powder diffracion of 1α (bottom - black), the experimetal one for it (middle - blue) and for the mixture of 1α and 1β obtained crushing 1α (top – violet and a image of 1β powder under white and UV-light). (d) Solid-state emission spectra of 1α (light green), 1β (pink) and 2 (aqua green) with the cromaticity graph.

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