Chemical versatility unsurpassed: ready access to long lasting lasers, bioprobes and light harvesters from BODIPYs

Enrique García Martínez de la Hidalga[1*], Clara Uriel[2], Ana M. Gómez[2], Jorge Bañuelos[1], Inmaculada García-Moreno[3], J. Cristobal López[2]

[1]Departamento de Química Física, Universidad del País Vasco-EHU, 48080 Bilbao, Spain.
[2]Instituto de Química Orgánica General, IQOG-CSIC, 28006 Madrid, Spain.
[3]Instituto de Química-Física "Rocasolano", CSIC, 28006 Madrid, Spain.

* *enrique.garcia@ehu.eus*

BODIPY (4,4'-difluoro-4-bora-3a,4a-diaza-s-indacene) dyes are in the forefront as modern fluorophores and are extensively applied in light driven devices and biophotonics. The reason of their success relies on the chemical versatility afforded by the boron-dipyrrin core ready available to a myriad of synthetic routes.[1] This feature allows a tailor made functionalization according to the target purpose and a deep modulation of their photonic properties. Accordingly, we have stablished a synthetic protocol to ameliorate them and endow multifunction.[2] Starting with alkylated commercial BODIPYs, the propargilation via Nicholas reaction at positions 2 and 6 leads to laser dyes with markedly improved photostability (no sign of degradation after 120000 laser pulses). From this scaffold and using click chemistry, conjugated BODIPYs and all-BODIPY triads are designed. In the former case, biomolecules as mannose and cholesterol were grafted at the BODIPY, which displays long lasting and bright emission (up to 80%) suitable for bioimaging probes. Alternatively, in the last case red-emitting BODIPYs were engaged with green-emitting BODIPYs leading to energy transfer cassettes. Regardless of the energy donor/acceptor ratio, these multichromophores display broadband absorption and highly efficient (up to 25%) red fluorescence (640 nm) and laser (710 nm) emission upon excitation/pumping at each chromophoric subunit owing to the ongoing intramolecular energy transfer.

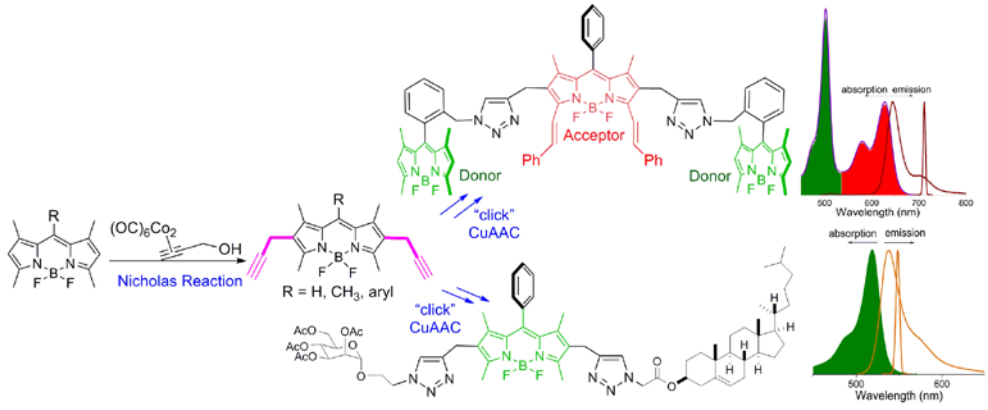

Figure. *Schematic view of the access to propargilated and conjugated BODIPYs, and cassettes.*

References

[1] N. Boens, B. Verbelen, M. J. Ortiz, L. Jiao, W. Dehaen *Coord. Chem. Rev.* **2019**, *399*, 213024.
[2] C. Uriel, A. M. Gómez, E. García Martínez de la Hidalga, J. Bañuelos, I. García-Moreno, J. C. López *Org. Lett.* **2021**, DOI: 10.1021/acs.orglett.1c02380.