Coupled Polymethine Dyes: A Palette of Possibilities

Benjamin Mourot[a]

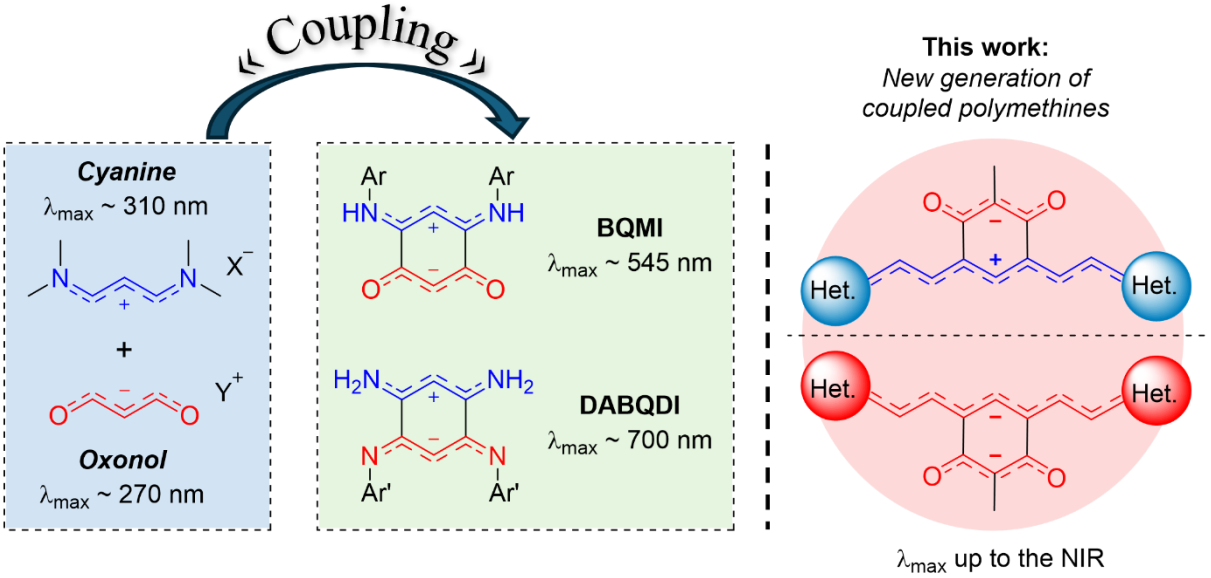
[a] *Centre Interdisciplinaire de Nanoscience de Marseille (CINaM), Marseille.*

benjamin.mourot@univ-angers.fr

Near-infrared (NIR) dyes play a vital role in a range of contemporary applications, including, but not limited to, biophotonics, energy conversion, and sensing technologies, owing to their structural tunability, which allows the tailoring of optical properties through a few synthetic steps. However, achieving strong NIR absorption and emission with organic chromophores typically requires the use of extended π–conjugated systems. This often results in poor solubility and increased molecular weight, thus limiting their practical use.

Polymethine dyes, commonly referred to as *cyanine dyes*, offer an attractive alternative due to their straightforward synthesis, tunable (hydro)solubility and generally low molecular weight. Upon molecular engineering (heteroatomic moieties, conjugation length, etc.), cyanine chromophores can be easily tuned to interact with NIR photons.[1] A seminal theoretical study by Dähne and Leupold in 1966[2] demonstrated that coupling of two polymethines units via a σ-bond leads to a significant reduction in the HOMO–LUMO energy gap, thus greatly affecting the dye's optical properties.[3]

Based on this coupling strategy, we have designed and investigated the electronic properties of a new class of extended coupled polymethines. These systems can adopt various electronic states, ranging from (di-)cationic, (di-)anionic or zwitterionic, depending on external stimuli, thereby offering a versatile platform for responsive NIR-active materials.[4,5]



(1) Bricks, J. L.; Kachkovskii, A. D.; Slominskii, Y. L.; Gerasov, A. O.; Popov, S. V. *Dyes Pigments* **2015**, *121*, 238–255.

(2) Dähne, S.; Leupold, D. *Angew. Chem. Int. Ed. Engl.* **1966**, *5* (12), 984–993.

(3) For a review, see: Mourot, B.; Jacquemin, D.; Siri, O.; Pascal, S. *Chem. Rec.* **2024**, *24* (12), e202400183.

(4) Mourot, B.; Mazan, V.; Elhabiri, M.; Sarkar, R.; Jacquemin, D.; Siri, O.; Pascal, S. *Chem. Sci.* **2024**, *15* (4), 1248–1259.

(5) Mourot, B.; Naim, C.; Siri, O.; Jacquemin, D.; Pascal, S. *Org. Chem. Front.* **2025**.