Optimized molecular materials for photonic applications in the near-infrared spectral range.

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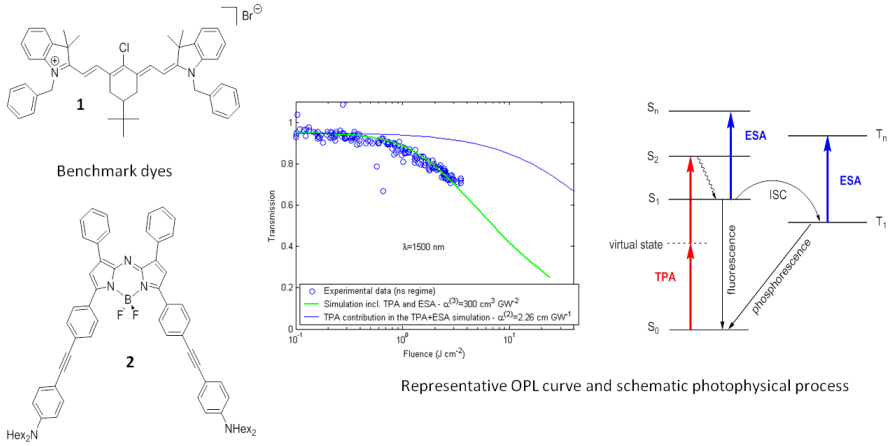
Optical power limiters are devices that are able to protect detectors (eyes, sensors…) against intrusive laser beams by limiting the transmitted intensity below the material damage threshold, while remaining transparent under low power irradiation. Such devices have already been widely developed to address visible (400-1000 nm) laser sources and are based on the nonlinear optical two-photon absorption (TPA) process. For one decade, a great research endeavor was focus on the extension of such devices to the near infrared spectral range up to 1500 nm and triggered the design a numerous chromophore featuring strong TPA in this spectral range. Our laboratory was involved since 2007 in this project and reported the design of polymethine and aza-bodipy dyes for this application.[1] Recently, we succeeded in the preparation of the first doped solid sol-gel material able to limit a laser beam at 1500 nm.[2]



Representative OPL curve and schematic photophysical process

This project is devoted to the optimization of this device using two main axes :

(i) The first axis is a formulation one that consists in mixing in the same material a combination of chromophore (aza-bodipy dyes) and gold nanoparticles in order to enhanced the two-photon absorption phenomenon by plasmonic effects.

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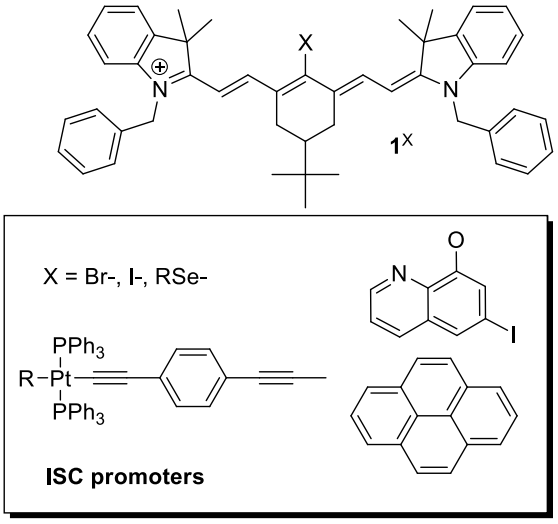
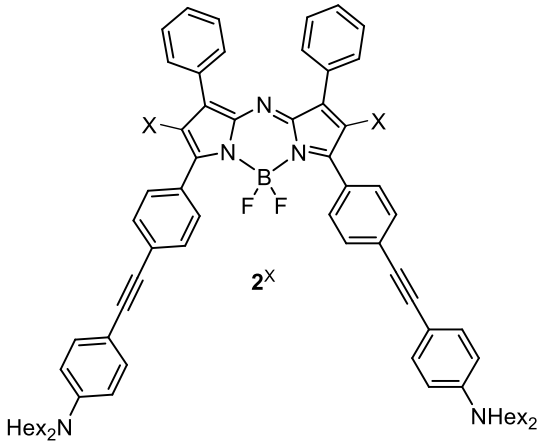
1 a) P.-A. Bouit, G. Wetzel, G. Berginc, B. Loiseaux, L. Toupet, P. Feneyrou, Y. Bretonniere, K. Kamada, O. Maury, C. Andraud, *Chem. Mater.* **2007**, *19*, 5325-5335; b) P.-A. Bouit, K. Kamada, P. Feneyrou, G. Berginc, L. Toupet, O. Maury, C. Andraud, *Adv. Mater.* **2009**, *21*, 1151-1154, c) P.-A. Bouit, C. Aronica, L. Toupet, B. Le Guennic, C. Andraud, O. Maury *J. Am. Chem. Soc.* **2010,** *132*, 4328-4335; d) S. Pascal, A. Haefele, C. Monnereau, A. Charaf-Eddin, D. Jacquemin, B. Le Guennic, C. Andraud, O. Maury *J. Phys. Chem. A* **2014**, *118*, 4038–4047.

2 Q. Bellier, D. Château, F. Chaput, K. Kamada, P. Feneyrou, G. Berginc, O. Maury, S. Parola, C. Andraud *J. Mater. Chem. C.* **2014**, *2*, 5105–5110.

(ii) The second axis is more fundamental and consists in the optimization of the excited state absorption process (ESA). Indeed, it has been well demonstrated in the visible range that a good spectral overlap between ESA and TPA at the incident laser wavelength can dramatically enhance the OPL properties.[3]

Whereas molecular engineering rules for TPA optimization are quite well established, less is known about optimization of ESA in particular in the NIR spectral range. However, it is generally recognized that increasing the exited state lifetime enhances ESA probability, and this consideration has triggered the development of chromophores in which the inter-system crossing (ISC) is favored, resulting in the population of a long-lived triplet excited state. **Therefore in this project, we plan to optimize the both TPA and ESA properties in the NIR spectral range**. To that end our benchmark chromophores **1** and **2**, will be substituted by heavy atoms like bromine, iodide, alkyl selenide or platinium acetylide fragment. Alternatively, poly-aromatic moieties known to stabilized triplet states in the 600-800 nm range e.g. acridine; hydroxyquinoline or more classically pyrene can be introduced by substitution of the fluoride atoms of the BF_2 fragment. In a more sophisticated approach, the two-photon antenna chromophores can be linked in a conjugated (or not) pathway to a central metalloporphyrine fragment acting as a central triplet promoting core.





This PhD student involved in this project must be highly motivated by the synthesis of these advanced chromophores and by the study of their photophysical properties. He will also be involved in the preparation of the sol-gel materials and will acquire some basics of nonlinear optical measurements.

[3] Q. Bellier, N. Makarov, P.-A. Bouit, S. Rigaut, K. Kamada, P. Feynerou, G. Berginc, O. Maury, J. W. Perry, C. Andraud *Phys. Chem. Chem. Phys.* **2012** ,*14*, 15299-15307.