Organometallics for optics

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My research activity focuses on the molecular engineering of organometallic complexes and coordination compounds, chromophores for luminescence, nonlinear optics, and photochromism. This molecular engineering of organometallic chromophores has allowed their use in optoelectronic devices such as OLEDs, LEECs, and DSSCs.
In addition, I am developing a collaboration on C-H activation catalysis (H. Doucet, J.-F. Soulé), which has proven essential for the development of new materials for optics: "*atom economy for energy economy*".

Design and synthesis of cyclometalated complexes (Pt, Ir): luminescence, photochromism, and Nonlinear Optics

1- Photochromism: Organometallic photochromes based on diarylethenes (DTE) have proven to be effective systems for modulating the optical properties of metal complexes.[1,2,3] We have explored the chemistry of photochromic DithienylEthene (DTE) containing N- ligands and their metal complexes (Zn(II), Ir(III), Fe(II) , Ru(II), Re(I), Pt(II)…) for the modulation of their optical, linear and nonlinear, properties.

2- Luminescence of Pt complexes: modulation of optical properties, organization, towards near-infrared emitters

The emission properties of square-planar platinum complexes, mono- and dinuclear, depend on the presence of π-π and/or Pt•••Pt interactions, resulting in emission in the near-infrared through the formation of excimers/aggregates. Platinum complexes, easily functionalizable, are therefore interesting molecular building blocks for developing strategies to control these intra- and/or intermolecular interactions.[4] Thus, new families of complexes have allowed the preparation of efficient OLEDs in yellow-green and deep red/NIR.[8]
Near-IR emitters are also potential candidates for bio-imaging. The development of efficient probes for imaging (collab. Pr. M. Massi, Perth, IRP CNRS) using complexes functionalized with bio-compatible substituents (sugars, amino acids, etc.) is also a goal. The complexes are studied as markers for tissue imaging, with a particular focus on brain tissue.[9]

3- C-H bond activation catalysis: an opportunity for the development of compounds with dedicated optical properties. H. Doucet (Rennes) and J.-F. Soulé (Paris Tech).

Functionalization of C-H bonds through catalysis is an opportunity to access new families of organic and organometallic luminophores. This approach, which enables access to original structures that are inaccessible through classical routes, makes syntheses easier and faster, and most importantly, more environmentally friendly.
In a first approach, we demonstrated the contribution of C-H bond functionalization for accessing i) compounds with fluorescence properties and ii) chelating ligands for the

preparation of new phosphorescent complexes. Subsequently, we developed Pd-catalyzed C-H bond functionalization directly on the coordinated 2-(difluorophenyl)pyridine/quinoline ligands of cyclometalated iridium(III) complexes. This novel strategy of " *C-H bond activation on-the-complex*" proved to be effective in introducing functional groups. [5,6,7]

We demonstrated the potential of C-H bond functionalization in boosting the luminescence properties of complexes of Ir(III).

The development of these syntheses for constructing photo-active molecules paves the way for the discovery of new organic synthesis techniques that can be widely applied across various fields.

1. V. Guerchais, J. Boixel, H. Le Bozec (*Book chapter*), "Linear and nonlinear optical molecular switches based on photochromic metal complexes" in *Photon-Working Switches*, Y. Yokoyama & K. Nakatani (Eds), Springer, 2017, Chapter 18.
2. J. Boixel, V. Guerchais, H. Le Bozec, D. Jacquemin, A. Amar, A. Boucekkine, A. Colombo, C. Dragonetti, D. Marinotto, D. Roberto, S. Righetto, R. De Angelis, *J. Am. Chem. Soc*. **2014**, *136*, 5367-5375.
3. J. Boixel, Y. Zhu, H. Le Bozec, M. A. Benmensour, A. Boucekkine, K. M. C. Wong, A. Colombo, D. Roberto, V. Guerchais, D. Jacquemin, *Chem. Commun.* **2016**, *52,* 9833-9836.
4. E. Garoni, J. Boixel,V. Dorcet, T. Roisnel, D. Roberto, D. Jacquemin, V. Guerchais, *Dalton Trans.* **2017**, *47*, 224-232
5. R. Boyaala, R. Touzani, T. Roisnel, V. Dorcet, E. Caytan, D. Jacquemin, J. Boixel, V. Guerchais, H. Doucet, J.-F. Soulé, *ACS Catalysis*, **2019**, *9*, 1320-1328.
6. R. Boyaala, M. Peng, W.-S. Tai, R. Touzani, T. Roisnel, V. Dorcet, Y. Chi, V.Guerchais, H. Doucet, J.-F. Soulé, *Inorg. Chem.* **2020**, *59*, 13898.
7. M. Peng, J. Lin, W. Lu, T. Roisnel, V. Guerchais, H. Doucet, J.-F. Soulé, *Chemistry - A European Journal*, 2021, 27 (49), 12552.
8. A. Colombo, G. de Soricellis, F. Fagnani, C. Dragonetti, M. Cocchi, B. Carboni, V. Guerchais, D. Marinotto, *Dalton Trans.* **2022**, *51*, 12161.
9. G. De Soricellis, F. Fagnani, A. Colombo, C. Dragonetti D.Roberto, D.Marinotto, D. H. Hartnel, .J. Hackett, M. Massi, B. Carboni, V. Guerchais, *Dyes and Pigments* **2023**, *210*, 111012.