

Ultrafast energy transfer in bis-porphyrin dyads

Hervé Dekkiche¹, Mary-Ambre Carvalho¹, Romain Ruppert¹, Laurent Ruhlmann¹,
Sébastien Richeter², Adam Langlois³, Paul-Ludovic Karsenti³, Pierre D. Harvey³

¹ Université de Strasbourg, Institut de Chimie, UMR CNRS 7177, 67000 Strasbourg, France

² Institut Charles Gerhardt, UMR CNRS 6253, 34095 Montpellier, France

³ Université de Sherbrooke, Département de Chimie, PQ J1K 2R1 Sherbrooke, Canada

E-mail: dekkiche@unistra.fr

Energy and electron transfers are key photophysical events in photosynthetic bacteria and plants. Synthetic models for these processes often use covalent linkers between the individual chromophores. Several metallo-bridged homo- and hetero-oligoporphyrins are reported in the literature and some of them showed significant electronic communication between the subunits.^[1] In our group, metalloporphyrins bearing one or two external chelating groups were used to build porphyrin dimers, dyads or larger assemblies (see Fig. 1). Strong electronic interactions were found in these architectures, as evidenced by electronic spectroscopy and electrochemical studies.

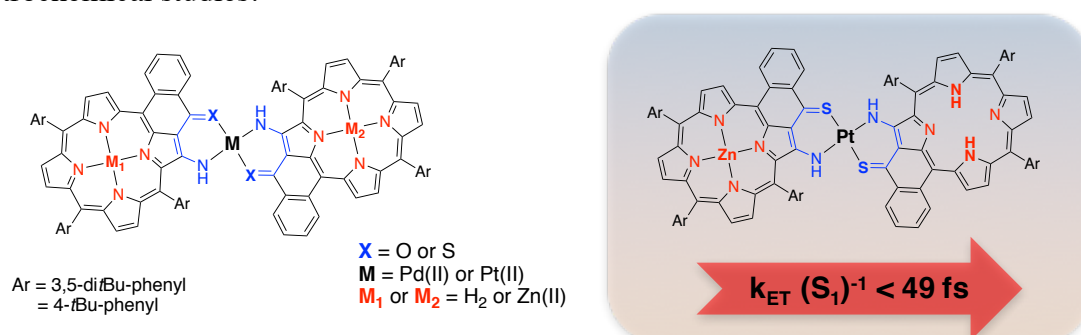


Figure 1. Porphyrin dimers and dyads (Zn(II)porphyrin-free base-porphyrin)

A few years ago, we have reported an energy transfer rate of about 650 femtoseconds (fs) in a bis-porphyrin dyad held together by a palladium(II) linker.^[2] Recently, homodimers and dyads were prepared with platinum(II) as linking ion and/or with a sulfur atom instead of oxygen in the chelating group. Their electrochemical and photophysical properties, supported by DFT calculations, were described and compared with earlier results.^[3]

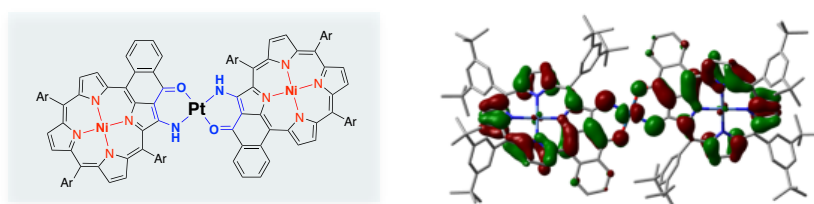


Figure 2. HOMO of a Ni(II)-Pt(II)-Ni(II) homodimer calculated by DFT.

It was shown that the electronic interactions between the porphyrin units were due to the molecular orbital overlap of the coplanar porphyrinic pi-systems with the d_{xz} metal center

orbitals (Fig. 2,3). An energy transfer faster than 50 femtoseconds (fs) was observed by fast transient absorption spectroscopy within the Pt(II)-sulfur dyad.

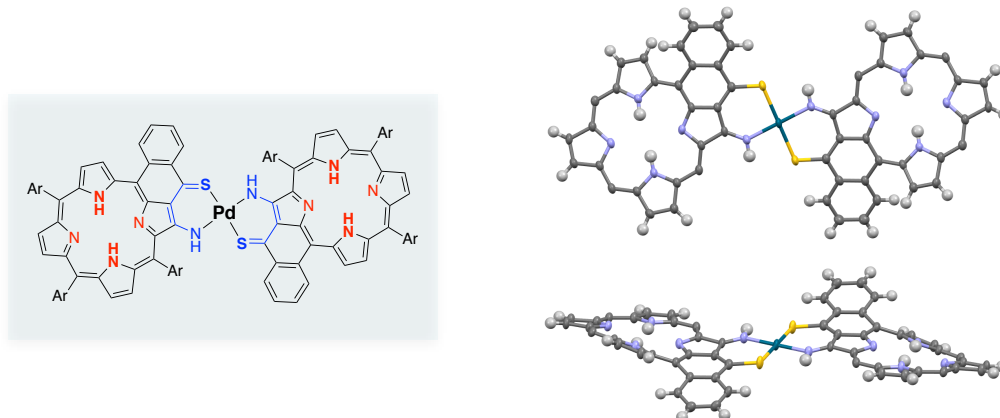


Figure 3. X-Ray structure of the free base-free base Pd(II)-Sulfur homodimer (3,5-ditBu-phenyl groups omitted for clarity)

Funding: Labex CSC (ANR-10-LABX-0026_CSC)

Acknowledgements: Thanks are due to the French Ministry of Research for a PhD fellowship (HD) and to the University of Strasbourg and the CNRS for continuous financial support.

References:

- [1] S. Richeter, C. Jeandon, J.-P. Gisselbrecht, R. Ruppert, H. J. Callot, *J. Am. Chem. Soc.* **2002**, *124*, 6168-6179. S. Yamaguchi, T. Katoh, H. Shinokubo, A. Osuka, *J. Am. Chem. Soc.* **2008**, *130*, 14440-14441. Y. Matano, K. Matsumoto, Y. Nakao, H. Uno, H. Imahori, *J. Am. Chem. Soc.* **2008**, *130*, 4588-4589.
- [2] M. Abdelhameed, A. Langlois, P.-L. Karsenti, S. Richeter, R. Ruppert, P. D. Harvey, *Chem. Commun.* **2014**, *50*, 14609-14612.
- [3] H. Dekkiche, A. Buisson, A. Langlois, P.-L. Karsenti, L. Ruhlmann, R. Ruppert, P. D. Harvey, *Chem. Eur. J.* **2016**, *22*, 10485-10493. H. Dekkiche, A. Buisson, A. Langlois, P.-L. Karsenti, L. Ruhlmann, P. D. Harvey, R. Ruppert, *Inorg. Chem.* **2016**, *55*, 10329-10336.