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Editorial

Preface to the special issue in honor of Monique M. Martin

This issue of the Journal of Photochemistry and Photobiology A: Chemistry is dedicated to Monique M. Martin, on the occasion of her recent retirement from CNRS, the French National Center for Scientific Research, within which she developed her outstanding scientific career. Monique Martin is a well-known photochemist who is one of the pioneers in France of ultrafast spectroscopy, particularly transient absorption spectroscopy, applied to the primary reactivity of organic molecules in condensed phase.

M. Martin was born in the small village of Ban-sur-Meurthe, in the Vosges province of France. She grew up in a modest family who imparted to her strong values of dedication to work, honesty and human respect that constituted the backbone of her dynamic attitude to the challenges of scientific research. After brilliant undergraduate and graduate studies in Physical Chemistry, Monique Martin started doctoral studies just at the time Ronald G.W. Norrish and Sir George Porter received the nobel prize in chemistry for the development of flash photolysis. Under the supervision of Lars Lindqvist, she studied the role of temperature and environment on the non-radiative transitions of xanthenic dyes by using the microsecond flash-photolysis technique. She earned her first PhD degree in physical chemistry in 1970, from universite paris-sud in Orsay, France. She then joined Prof. Lindqvist's group, at the laboratory of molecular photophysics, as a CNRS research associate (Attaché de Recherche) and received her doctoral thesis (Doctorat d'État) in 1974, pursuing her study of the non-radiative processes of xanthenic dyes in solution with, in particular, an original contribution on the role of the dye-solvent hydrogen bonding interaction on the photodeactivation rate of these dyes.

On a professional leave M. Martin could join William Ware's group, at the University of Western Ontario, London, Canada, between 1975 and 1976. As a research associate she carried out postdoctoral studies on the fluorescence quenching of carbazole by pyridine and substituted pyridines, that is, on the radiationless processes in carbazole-amine hydrogen-bonded complexes, using nanosecond single photon counting method.

Back from Canada, Monique Martin pursued, for a few years, research on two-photon dissociation as well as triplet photophysics of carbazole, using flash photolysis. However, eager to learn new developing techniques and to collaborate with one of the greatest photochemists of all times, she decided to spend six months in Noboru Mataga's group, in Osaka University, Japan, in 1981. She could on this occasion apply picosecond transient absorption spectroscopy to understand the deactivation processes of excited hydrogen-bonding complexes by intermolecular electron transfer. In particular she showed in the case of the 7H-dibenzocarbazole-pyridine complex that an equilibrium could be reached between the LE (locally excited) state and the CT (charge transfer) state in less than 10 ps. She later demonstrated that hydrogen bonding with pyridine lowers the photoionization threshold of dibenzocarbazoles in solid solution. Her stay in Osaka allowed Monique Martin to build a, lifelong relations of friendship and respect with N. Mataga and a number of his now famous coworkers, among which Tadashi Okada, Hiroshi Masuhara and Hiroshi Miyasaka.

Another important consequence of her stay in Japan was that Monique Martin became forever a carrier of the virus for ultrafast spectroscopy! Back to France she tried to implement picosecond spectroscopy in her laboratory and finally, given the high cost of the commercial laser systems, opted to associate with a highly talented physicist, Yves Meyer, to build a picosecond laser system from scratch. This decision led Monique Martin into the realm of laser physics, which she concomitantly discovered, mastered and applied to her goal. After a few years of struggle, M. Martin and Y. Meyer could demonstrate a completely new tunable sub-picosecond laser source, based on non-conventional concepts. This homemade source was associated with a pump-probe transient absorption set-up, equipped with broadband continuum probing and providing time resolution of about one picosecond.

Such "tour de force" allowed Monique Martin to investigate in the nineteen eighties photochemistry through a study of the ultrafast primary processes at work in organic systems in solution. Attracted by the fascinating photonic properties of malachite green (a short-lived saturable absorber used in the Meyer-Martin laser), Monique Martin started a research program on the fast deactivation mechanism of tri- and diphenylmethane dyes (molecular rotators), the fluorescence quantum yield of which are highly dependent on solvent viscosity. She extended this research to various compounds containing rotatable electron-donating anilino substituents, including triphenylphosphines (collaboration with Wolfgang Rettig, Berlin), the merocyanine DCM and the most debated DMABN (dimethylaminobenzonitrile; indirect

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collaboration with James T. Hynes, University of Colorado, Boulder). She could demonstrate in all cases that the excited-state relaxation involves the formation of an emissive or non-emissive intermediate state. The dependence of the observed kinetics on solvent viscosity, polarity, solvation time supported a common mechanism involving photoinduced charge transfer coupled with structural change. Monique Martin had by that time been promoted CNRS Director of Research.

Her interest in intramolecular charge transfer further led M. Martin to a fruitful association with Bernard Valeur (Conservatoire National des Arts et Métiers, Paris) to study the reversible photorelease of metal cations (Li^+, Ca^{2+}...) complexed to DCM-crown, a fluoroionophore made of a monoaza-15-crown fused to the laser dye DCM, which she proved by transient absorption spectroscopy. She similarly collaborated with Mireille Blanchard-Desce (Université Bordeaux 1, France) on the photophysics of push-pull polyenes, specially designed for organic-based nonlinear optics.

By the end on the nineties Monique Martin was invited by Christian Amatore to join the department of chemistry of Ecole Normale Supérieure (ENS) in Paris, in order to introduce laser photophysical chemistry to the department. In 2000 she implanted there a new laboratory of ultrafast photochemistry, equipped with a 50 fs laser source and corresponding broadband transient absorption spectroscopy setup. This change of academic institution was the occasion for Monique Martin and her co-workers (Pascal Plaza, Pascale Changenet-Barret and later Christian Ley) to reorient their research towards photobiology, more precisely the understanding of the primary photoinduced processes in photoactive proteins, and the goal of designing bio-inspired photofunctional materials.

The first interest of Monique Martin's group was focused on PYP, the Photoactive Yellow Protein, believed to trigger the phototactic response of a bacterium via the ultrafast *trans-cis* isomerization of its covalently-bound chromophore (a *p*-coumaric thioester). Several studies in collaboration with the group of Ludovic Jullien (ENS, Paris), evidenced that the behavior of analogues of the PYP chromophore highly depends on the electron donor-acceptor character of the molecule and showed that the thioester derivative does not undergo *trans-cis* isomerization is solution. The riddle was then to understand why the same molecule isomerizes within the protein. This was finally rationalized in terms of rigidity of the protein nanospace containing the chromophore, which hinders one of its nonradiative deactivation routes (rotation of the phenolate moiety) and thereby favors photoisomerization. These concepts allowed Monique Martin and Jean-Maurice Mallet (ENS, Paris) to design a first model of the PYP active based on a β-cyclodextrin caging the PYP chromophore, which was proven to favor the photoisomerization route.

In collaboration with Francesco Lenci (CNR, Pisa), Monique Martin also studied the primary reaction of OBIP, a protein thought to be involved in the photophobic response of a protozoan and non-covalently binding a chromophore, oxyblepharismin. Despite the difficulty of not knowing the structure of the protein, it was shown that ultrafast photooxidation of oxyblepharismin is at the heart of OBIP's photoreactivity. It was however suggested that this reaction might only play the role of a sunscreen for the protozoan, rather than being the trigger of its photophobic response.

Last but not least, Monique Martin initiated collaboration with Chris Bowler (ENS, Paris) on proteins of the cryptochrome/photolyase family. Her group specifically studied the so-called photoactivation reaction, which allows the flavin adenine dinucleotide cofactor (FAD) of these proteins to be photoreduced. They showed that initially oxidized FAD is photoreduced in about 0.5 ps by a nearby tryptophan residue, and that the corresponding hole migrates, via an intermediate tryptophan, towards a third distant tryptophan in the picosecond regime.

It should not be forgotten that Monique Martin maintained an activity in the field of "non-biological" photochemistry through her long-lasting collaboration with B. Valeur. They recently brought final proofs and mechanistic details of the photorelease of Ca^{2+} from DCM-crown and demonstrated the feasibility of a new type of light-driven molecular shuttle, performing photoinduced cation translocation through a calix[4]arene tube.

This preface will be closed mentioning that Monique Martin was committee member of the physical chemistry division of the French society of chemistry, scientific committee member of the international conference on photochemistry as well as former organizer and committee member of the international conference on femtochemistry. She was member of the international advisory editorial board of chemical physics letters and European editor of Journal of Photochemistry and Photobiology A: Chemistry.

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