

**PHOTONIQUE MOLECULAIRE:  
MATERIAUX, PHYSIQUE ET COMPOSANTS**  
*MOLECULAR PHOTONICS: MATERIALS, PHYSICS AND DEVICES*

**Foreword**

Molecular photonics is an emerging field of research, at the strategic intersection of chemistry, physics and engineering sciences, these three closely interacting areas providing a most fruitful background and avenue for the development of photonics. By drawing on the fundamental advantages of molecular systems to be illustrated in this issue, the main topics of this domain can be defined as two-fold: firstly, to stimulate fundamental advances in our understanding of light–matter interactions in molecular media with implications in both the physical and chemical sciences; and secondly, to provide a wealth of innovative propositions to renew concepts and functionalities in optoelectronics, for the telecommunication industry and beyond, with current advances pertaining increasingly to biotechnologies. Indeed, this research is strongly motivated by the need for progress in optical signal processing functions and devices at a rate in-keeping with the development of broad band time or wavelength division multiplexed systems at present essentially based on inorganic materials. These innovations also start to have a strong impact on biotechnology, with the growing use of luminescence and nonlinear functional molecules in advanced imaging and diagnostics techniques at the scale of the cell or even down to its macro-molecular components.

The object of this special issue is to illustrate some advances in this emerging field of study, with emphasis on a selection of essential ingredients which are actually enabling genuine progress in this field, with equal emphasis on strongly interconnected conceptual and practical aspects. These can be broken down into four major domains which concentrate current and foreseeable driving forces in molecular photonics, namely:

- *Chemistry*, and in particular, organic synthesis, targeted and governed by the continuously updated rules of molecular engineering.
- *Physics*, which provides a broad range of applicable properties and jointly contributes to a better understanding of light–matter interactions at different scales. Hand in hand with chemistry, physics plays a major role in ‘simplifications’ and in the definition therefore of molecular templates to guide and rationalize synthesis towards relevant targets. Within a wealth of molecular solutions that might end-up being otherwise embarrassingly abundant and possibly frightening to atomic or semiconductor solid-state physicists, this rationalizing partnership between physicists and chemists has been the cornerstone of this field. It continues to be more than ever a major driving force in the field, now increasingly, and no less fruitfully, enlarged to life sciences.
- The development of *advanced instrumentation*, such as illustrated in this volume, allows us to actually visualize, probe, measure, a diversity of phenomena as well as manipulate or fabricate functional objects, both at unprecedented space–time dimensions reaching the size of individual molecules and durations down to the limit of a cycle of light radiation.
- The coming to maturity of viable *molecular technologies* allowing us to elaborate organic photonic devices, which opens the way to promising industrial opportunities and will unavoidably come to complement and challenge current purely inorganic semiconductor based solutions.

These four areas of study provide a coherent backbone to the progress of molecular photonics and form an ‘offer’ which can sometimes anticipate the ‘demand’ of the day, the latter being very often curtailed by

the limits of the earlier state-of-the-art, especially at a time when fluctuations of industrial and economic factors may not be in favour of innovation.

The different articles of this special issue are basically meant to hopefully provide material and solid ‘no-nonsense’ arguments based on factual demonstrations to support these advances without, however, pretending to cover exhaustively such a vast field of research.

*Chemical aspects* include molecular engineering and the synthesis of organic systems in the broadest sense (purely organic molecules, organo-minerals, dyes and polymers, hybrid materials, single and liquid crystals, etc.) displaying useful properties, further optimised for the large class of phenomena pertaining to light–matter interactions: quadratic and cubic non-linear optics, one- and two-photon pumped luminescence, laser effects, photoinduced transformations such as pertain to photochemistry, photo- or electric-field-induced charge transport, photovoltaics, etc. To these primary requirements one must add the no less essential and challenging constraints of stability and optical quality. Compatibility with fabrication constraints and applications in a realistic environment are also integrated, jointly, at the different levels of molecules, materials and devices, into the ‘specifications’ which are prerequisite to an actual device.

*Physical phenomena* will be hereafter essentially related to nonlinear effects and lasers, which draw from the structure and properties of the constituent molecules, and are amenable either to a classical or quantum picture of light–matter interactions depending on the scale and phenomenon of interest. These include propagation phenomena, 1D, 2D or 3D (light localization) confinement, modal or spectral resonances depending on the geometric or physical configuration of the active material; with organic microcavities and the growing domain of photonic crystals provide important illustrations with special advantages to be derived from organics. The experimental configuration considered (for example, the nature of the laser source, wavelength and pulse duration) or the size of the interaction volume, be it a bulk material, structures at the wavelength scale, nanostructures down to the scale of ‘single’ molecules, are also compelling factors controlling the nature, efficiency and potential applications of physical phenomena.

The development of an advanced *photonic instrumentation*, by no means an ancillary domain, has accompanied and truly enabled the development of molecular photonics, for example the use of ultrashort-pulse intense laser sources, optical parametric oscillators with coherent tuneable emission to probe resonant configurations. New types of microscopies (confocal, multiphotonic, near field, etc.) have allowed the mapping of different photonic properties much beyond the boundaries set by the Rayleigh criterion, allowing us to now reach the size of single molecules and the revolutionary ability to actually visualize at an unprecedented level of precision. This field of study has seen remarkable breakthroughs in biophotonics, where the tracking of fluorescent genes across a cellular environment has become almost as routine as classical microscopy in many biological laboratories.

*Technological developments* are bound to have the strongest impact on industrial users, essentially in optical telecommunications, where such vital components as high rate modulators (some tens of Gbits/s or more), switches, frequency converters, in particular from optics to the microwave range, active add–drop filters, all based on organics and polymers in the 1.55  $\mu\text{m}$  window, open the possibility of large volume and low cost production facilities as well as the availability of new broadband services with strong and still largely unforeseen social impacts. In particular, progress towards a viable technological pathway, based on electrooptic polymers, as discussed in the last article of this issue, is bound to lead to an organic integrated optical circuitry fully compatible with inorganic semiconductors. That same technology is leading to the development of new microlaser sources based on different dyes and polymers targeted towards solid-state luminescence, emitting for the moment in the visible or near infrared, with an increasing shift towards the near infrared telecom window.

The aim of this issue is to draw to the attention of a large readership to the advantages to be gained from the challenging possibilities of molecular photonics: whereas organic materials may have been traditionally objected to because of a certain lack of robustness, a ‘drawback’ somewhat inherent to their otherwise advantageous flexibility, increasingly credible solutions have come to strengthen and stabilise these materials, thus somewhat outdating the earlier prejudice. Possibly more interesting for the future

is to face this flexibility upfront and view it as a rather unique asset: indeed, building-up on the many unfrozen degrees of freedom of molecules and molecular assemblies allows us to further engineer an additional layer of diverse static or dynamical characteristics, inaccessible to classes of more rigid materials such as single crystals. Such flexibility may in a way then become a decisive advantage, whereas the robustness of mineral crystals may appear in contrast as a technological liability, both costly and limiting when it comes to ‘intelligent’ and adjustable materials. It is nevertheless essential to take advantage of the remarkable progress made in the last decade in stabilising organic materials, a requirement now integrated in the ‘specifications’ at the same priority level as the primarily targeted physical effects. Over and above this legitimate requirement, guaranteeing a greater credibility for the emerging field of molecular photonics in view of the comparison with already existing and more mature inorganic avenues, one has to learn to manage the compromise between flexibility and robustness, which is at the heart of molecular photonics. Such an evolution can also be seen at the level of physical properties, with a strong and original impact on fabrication technology: optical manipulation of molecular objects in solid-state films has already been mentioned as an example and will be illustrated in this issue by way of a most striking implementation of a coherent control approach, somewhat in contrast with more mainstream developments in this field which is traditionally bearing on the simplicity, however limited functionality, of atoms or small molecules. This renewed approach is currently enabling the formation of sophisticated spatial patterns with new photonic properties unattainable from crystals. Elsewhere, the growing use of ‘soft technologies’ specific to organic materials beyond present day traditional technologies which are mainly extrapolations of current inorganic semi-conductor optoelectronics, promises the emergence of truly low-cost, high-volume production methods, as demanded by the market. This new era would reflect an important land-marking stage, quite ubiquitous in the learning process. One will have passed the necessary, but transitional stage of imitating already existing state-of-the-art, essentially inorganic, technologies, onto the more mature stage, one might want to simply call it adulthood, whereby the inherent and unique qualities of the field are being now confidently cultivated *per se*, not worrying too much anymore about imitation or competition. In this new phase, such characteristics once frowned upon as the supposedly inherent fragility of organics, their sensitivity to the environment, a somewhat embarrassingly broad pool of structures, once identified, addressed and creatively exploited, will increasingly appear as unique and highly positive assets rather than burdening liabilities. At some point, and it is the editor of this review’s belief that we have reached some sort of break-even point in this domain, far from having to fight and contradict such ‘drawbacks’, one will have to promote, and optimize their so far largely untapped potential, furthermore with the help of mother nature which is always good to have on one’s side.

This special issue will be useful if it manages to also convince the reader that we are today standing at this transition stage, based on actual progress and not any sort of belief, as I believe is amply illustrated throughout the various articles covering in their own ways major aspects of the four cornerstone fields mentioned above.

A most pleasant and important conclusion is to thank warmly my colleagues who have co-authored various contributions for their efforts, and willingness to share both some review perspectives and their visions, together with up-to-date results, not an easy blend indeed, and moreover for having largely set, throughout decades for some of them, the high standards of this field as well as having defined and constantly updated its challenging directions. As in any worthwhile enterprise, which, all said and told, essentially boils-down to a human adventure, let me add my conviction, without hopefully upsetting anyone, however brilliant his earlier achievements, but rather as a further call to the talent and creativity of currently active researchers in the field and as the undisguised desire to see many more newcomers enrolled, that the better is still to come.

**Joseph Zyss**  
**Laboratoire de photonique quantique et moléculaire and Institut d’Alembert**  
**École normale supérieure**  
**Cachan, France**