Will the 21st be the century of photonics?
An organic and bio-inspired materials perspective

F Cacialli

Materials with new or advanced and, crucially, "functional" properties have always been drivers of societal change, as underlined by the conventional naming of the various "ages" (stone, bronze, iron…), so that the question arises as to what materials could underpin photonics in the 21st century, ideally enabling a "photonics revolution" similar to the microelectronics one, underpinned by semiconductors in the last century.

Photonic applications for light generation, transmission, modulation and detection are very much at the forefront of industrial and academic interest as key enabling technologies (https://ec.europa.eu/programmes/horizon2020/en/h2020-section/photonics), and have already been substantially developed over the last 60 years, mostly on the back of the development of the inorganic semiconductors, but there is a perception that we might have only seen the tip of the iceberg, and that novel and more performing materials are still needed to fulfil the full potential of photonics.

Within this context, a cutting-edge insight into organic, biological and bio-mimetic materials for photonics has been provided by the papers presented at the European Materials Research Society (E-MRS) symposium: "Advanced materials and architecture for organic, printable and bio-inspired photonics", held in Strasbourg from 20th to 22nd of June 2018.

I am delighted to be able to introduce a selection of such papers in this special issue of Advanced Functional Materials that also includes additional invited contributions from leading scientists active in this field.

Clearly, "organic semiconductors" have become the subject of intense industrial and academic investigation near the turn of the millennium. Not only do these powerfully combine the semiconductors and plastics breakthroughs of the last century, but are also suited for applications spanning from optoelectronics to photonics and have their most obvious champions in the (arguably) best quality displays on the markets.

Such materials are soft, solution processible, and akin in many ways to materials of biological origin, whose salient properties, often particularly relevant to photonics, can also be harnessed via so-called bio-mimetic approaches. Solution processability and/or printability are also desirable properties for essentially inorganic semiconductors such as perovskite-like ones, that offer new frontiers for both photovoltaics and light-emitting applications, and that have thus commanded inclusion in this special issue.

Within this context, and because of the arguably unparalleled historical and societal significance of paper, I would like first of all to draw attention to three contributions (one review and two full papers) highlighting the opportunities provided by cellulose in its various forms.

A current and very significant technological challenge, for example, somewhat also hampering deployment of so-called internet-of-things, IOT, is that of providing "cheap" energy to all the devices expected to surround and accompany us in increasing numbers (~ trillions according to initial estimates). The comprehensive review by Brunetti, Brown, and collaborators (art. N. 1806798) on printed solar cells and energy storage devices on paper thus provides a much-needed update on recent progress in dealing with the challenges presented by paper porosity and permeability in the fabrication and operation of solar cells and energy storage devices on this cheap, flexible, recyclable, and non-toxic material. The demonstration of photovoltaic diodes (PVDs) on paper with power conversion efficiency

(PCE) of 13% or higher and of paper-based supercapacitors and batteries with maximum achieved capacity of 1350 mF cm^{-2} and 2000 mAh g^{-1}, is extremely promising therefore, and the thorough review presented here is likely to serve as an extremely useful reference for all those already working in, or planning to enter, this challenging but rewarding area.

Not only is cellulose cheap to produce, and benefitting from millennia of technological development, but also inherently "photonic", as comprised of fibers that self-organize on a subwavelength scale in (chiral) cellulose nanocrystals (CNC), and that can thus provide structural color, or circularly polarized transmission/reflection. Vignolini and collaborators (art n. 1804531) report for example on a method to fabricate responsive photonic CNC arrays with superior optical uniformity, scalability, and efficiency, with the scope to remove barriers to adoption of CNC-based materials in cosmetics, interactive pigments, as well as anticounterfeit applications.

In another inspiring example of how cellulose optical/nanostructural properties can be exploited, Pereira, Grey and collaborators (art. n. 1805279) leverage instead the chirality of the CNC, to demonstrate photo-transistors with distinct sensing properties for left- and right-handed circularly polarized light. These are fabricated simply by infiltrating sodium ions into films of CNC with a left-handed internal long-range order, so as to yield solid-state electrolytes then used as the gate dielectrics in inorganic transistors that incorporate amorphous indium–gallium–zinc oxide (a-IGZO) as the (blue-light) photosensitive semiconductor.

Phototransistors (PTs) are of general importance in optoelectronics (and photonics), because, with respect to photodectors, inherently provide the possibility of amplification, on top of detection, thereby potentially achieving superior sensitivities. The contribution by Köhler and collaborators (art. n. 1805684) of an organic bidirectional PT is then a consequentially interesting reading, especially as in addition to bidirectional PT action the authors demonstrate the realization of basic logic elements like NOT-, AND-, and OR-Gates, which may provide the basis for digital applications.

Taking "detection" into the high-energy photons arena, an intriguing paper by Fraboni, Ciavatti and collaborators (art. n. 1806119), discusses recent improvements in the use of organic field-effect transistors (OFETs) for sensing of X-rays. This is based on careful engineering of the active materials by functionalisation of the materials with Ge atoms, so as to increase the atomic weight (with respect to C and Si, e.g. with respect to archetypal compounds, such as so-called TIPS-pentacene) and thus the X-rays scattering cross-section, while concomitantly achieving mechanical flexibility, and large area processing. It is easy to see the implications that this research may have for biomedical and diagnostic applications.

Organic chemistry's endless flexibility for tailoring of the active materials is one of the advantages of organic over inorganic semiconductors, and this powerfully comes across in the review paper by Moser, McCulloch, and collaborators (art. n. 1807033). This contribution describes recent approaches to design and synthesis of materials for organic electrochemical transistors that exploit the coupled nature of ionic and electronic transport to achieve superior transduction compared to "conventional" OFETs, and that hold particular promise for detection of biological analytes (bioelectronics). The review provides a good account of how better understanding of the structure–property relationships of the various channel materials has allowed a tenfold improvement of the transducing ability, and crucially inspires design guidelines of future materials with the scope to address the challenges in the field.

One of the most relevant and potentially high-impact goals of bioelectronics is of course the provision of suitable "active" prosthesis. The contribution by Schiek, Abdullaeva and collaborators (art. n. 1805177) is a case in point, giving a marvelous example of how organic semiconductors provide credible prospects for novel electrically self-sufficient photovoltaic

prosthetics for neurostimulation, especially for restoration of light sensitivity in degenerated retina.

In addition to prosthetics, organic bioelectronics and photonics are expected to provide solutions to detection of significant analytes, e.g. by providing cheap printed platforms integrating light sources and detectors across microfluidic channels in which the biological fluids might be forced. To ensure selectivity and sensitivity one of the prerequisites for either sources and detectors is spectral purity. Interestingly, judicious exploitation of the "supramolecular chemistry portfolio" can significantly contribute to this challenge, as elegantly demonstrated by Würthner, Liess and collaborators (art. n. 1805058). They provide a clear demonstration of how covalent functionalisation of the same "backbone" chromophore with substituents presenting different degrees of bulkiness and rigidity can direct non-covalent interactions and thus self-assembly of the monomers towards formation of either H or J aggregates. In practice, this understanding enables a simple route to unprecedented wavelength-selective photodectors with maximum external quantum efficiencies of up to 11% and ultranarrow bandwidths down to 30 nm.

With a view to achieving narrowband emission, it should be noted that J-aggregates' microcrystalline nature and coherent exciton migration generally result in strong nonradiative exciton recombination at the grain boundaries that diminish the photoluminescence quantum yield. However, in a complementary contribution, Heier, Mahrt, and collaborators (art. n. 1806997) demonstrated two distinct routes using surface-guided molecular assembly to grow different J-aggregate morphologies like platelets and lamellar crystals with improved crystallinity which affords a concomitant reduction of nonradiative decay and improved photoluminescence efficiency.

Of course bandwidth control and manipulation, one of the fundamental aims of photonics, may also be pursued by engineering of the materials refractive index, as powerfully demonstrated by Stingelin, Stavrinou and collaborators (art. N. 1808152), that incorporated a low refractive index fluoropolymer and a very high refractive index titanium-functionalized polyvinyl alcohol derivative to produce antireflection coatings (ARCs) and distributed Bragg reflectors (DBRs) with 88% reduction in reflectance across the visible compared to uncoated glass, and fully solution-coated DBRs with a reflection of >99% across a 100 nm spectral band in the visible region.

Another aspect that is potentially important for application of organic (bio)electronic devices to detection of a variety of analytes (e.g. in point-of-care applications) is the extension of the emission and detection range into the near-infrared (NIR) region of the electromagnetic spectrum, considered that many biological compounds of interest have absorption bands in this region. This is in fact a significant challenge, owing to the combined effects of aggregate-quenching (mainly H-aggregates) favored by the extended planar molecular configurations needed to lower the energy gap, and of the so-called "energy-gap" law, as explained in the comprehensive review by Zampetti et al. (art. n. 1807623). Despite the hurdles mentioned above significant achievements have been obtained recently in this area as well which is of particular interest for bio-applications, given the semitransparency of biological matter in this particular spectral window, but that also offers opportunities for through-space, short-range communications, night vision, and more generally security applications to name but a few. This works also offers significant insight into the fundamental photophysics of organic semiconductors as well as of their derivatives and analogues, that require ever increasing sophisticated techniques for their investigation.

One of these spectroscopic techniques is the so-called three-beam pump–push–probe (PPP), now a well-established tool for investigating the multidimensional configurational space of a molecule, as it allows probing of the multiple and often complex deactivation

pathways of the excited molecule. In their compelling contribution, Lanzani, Paternò and collaborators (art. n. 1805249) clearly show how PPP can also be used to achieve ultrafast all-optical switching in π-conjugated systems, as exemplified in the case of a newly synthesized nanographene molecule with superior photo- and environmental and stability.

Although prone to degradation and less performing than some of the inorganic materials, e.g. in comparison to Pb-based perovskite ones, that have recently shown tremendous photovoltaics performance and very promising results as light emitters and photonic materials in general, one big advantage of organics is their relatively low toxicity or even biocompatibility. The contribution by Petrozza, Manna, and collaborators (art. n. 1805299) has therefore a special importance, as it reports on a thorough spectroscopic study of emission from newly synthesized 0D lead-free colloidal $Cs3Bi_2I_9$ perovskite nanocrystals, whose emissive states and relative dynamics are also hotly debated. Here, they they found that one of their most interesting features, i.e. their broadband emission, is afforded by the coexistence of emissive excitons and sub-bandgap emissive trap-states.

Last but not least, Farinola, Trotta and collaborators (art. n. 1805521) give an exciting and extensive account of how certain types of bacteria can also provide a source of materials for optoelectronics and/or photonic devices and venture into discussing potential applications of the latter in solar energy conversion and storage, as well as in light information technologies. Their comprehensive review considers the use of both photoactive cellular components and entire living cells thus pointing at how extended the scope might be in shifting the paradigm of design and synthesis of materials and devices for optoelectronics should these approaches be developed to the full.

In concluding, I would like to thank the authors for providing their contributions, as well as Dr Riboni and all the Advanced Functional Materials staff for their fantastic support.

It is not quite so clear yet if the 21st will be the century of photonics, but I very much hope that this necessarily limited selection will be both representative of some of the most advanced approaches and achievements obtained so far, and most importantly that it will be a source of inspiration for the increasing community of those using novel, supramolecular, and biological or biomimetic materials for photonics.