Chem Soc Rev

This article was published as part of the

Hybrid materials themed issue

Guest editors Clément Sanchez, Kenneth J. Shea and Susumu Kitagawa

Chem Soc Rev

Dynamic Article Links

Cite this: *Chem. Soc. Rev.*, 2011, **40**, 886–906

www.rsc.org/csr

CRITICAL REVIEW

Hybrid materials for optics and photonics†

Benedicte Lebeau[a] **and Plinio Innocenzi***[b]

Received 14th September 2010
DOI: 10.1039/c0cs00106f

The interest in organic–inorganic hybrids as materials for optics and photonics started more than 25 years ago and since then has known a continuous and strong growth. The high versatility of sol–gel processing offers a wide range of possibilities to design tailor-made materials in terms of structure, texture, functionality, properties and shape modelling. From the first hybrid material with optical functional properties that has been obtained by incorporation of an organic dye in a silica matrix, the research in the field has quickly evolved towards more sophisticated systems, such as multifunctional and/or multicomponent materials, nanoscale and self-assembled hybrids and devices for integrated optics. In the present *critical review*, we have focused our attention on three main research areas: passive and active optical hybrid sol–gel materials, and integrated optics. This is far from exhaustive but enough to give an overview of the huge potential of these materials in photonics and optics (254 references).

1. Introduction

Very soon after the rise of sol–gel chemistry as a new research field in 1980s[1,2] the soft conditions of sol–gel processing have been identified as an important opportunity to introduce organic species within an inorganic glassy network.[3] Moreover, sol–gel chemistry offers the possibility of an easy shape-modeling, which is of high interest for several applications. The pioneer work of David Avnir's group remains a key step in the history of materials research;[4] they showed for the first time that sol–gel chemistry allows preparing inorganic glasses doped with organic dyes that preserved their optical activity after incorporation within the matrix. After the example of Avnir, several organic and biological species have been incorporated within sol–gel oxide matrices and since then hybrid sol–gel chemistry has widened its fields of application to optics and photonics, medical and sensor devices, and protection coatings. The first researches dedicated to the elaboration of hybrid organic–inorganic materials have rapidly identified most of the advantages and the drawbacks of sol–gel chemistry. In particular it was soon demonstrated that the interaction between incorporated organic species and their surrounding chemical environment is the main key point to optimize a hybrid matrix in terms of structure, texture and specific properties.[5] This is also the reason why the type of interaction existing between the organic and inorganic components has been used to classify hybrid materials.[6] On this basis we can basically identify two classes of hybrids, in the first class the organic molecules have only weak interactions through secondary bonds to the matrix, in the other case there is a direct covalent link through a non hydrolysable Si–C bond. This is a quite rough classification, the first case falls, in fact, within the more general group of molecular scale composites and only in the second group we could identify truly hybrid materials; this division, however, identifies quite well the difference between materials that in several cases can exhibit very similar functional properties but whose intimate structure can be very different.

The chemical route that is chosen for incorporation of the organic component still represents the core issue for a successful processing of hybrid materials and several strategies have been developed so far.[7,8] The most common dye incorporation methods are doping or covalent bonding which are realized *via* an *in situ* process or a post-synthesis treatment. The *in situ* methods consist in the introduction of the active species in the reaction medium while the post-synthesis approach is either realized in solution or by wet impregnation. For optical applications, dye doping by an *in situ* method or post-synthesis wet impregnation has rapidly showed its limits such as low loading rates and inhomogeneous dispersion. The weak interactions generated in this latter case are an advantage when high mobility is preferable (*e.g.* fast reversible photochromism) but they represent a drawback when low mobility is expected, such as in materials with second-order non-linear optical properties. Strong interactions such as covalent coupling are in general preferred when high and controlled loading is desired; the organic component can be covalently linked to the inorganic backbone by post-synthesis grafting or by direct synthesis. The latter method is generally preferred since it

---

[a] *Equipe Matériaux à Porosité Contrôlée, Institut de Science des Matériaux de Mulhouse, CNRS LRC 7228, UHA-ENSCMu, 3 rue Alfred Werner, 68093 Mulhouse cedex, France*
[b] *Laboratorio di Scienza dei Materiali e Nanotecnologie, D.A.D.U., Università di Sassari and CR-INSTM, Palazzo del Pou Salit, Piazza Duomo 6, 07041 Alghero (Sassari), Italy. E-mail: plinio@uniss.it*

† Part of the themed issue on hybrid materials.

allows a more homogeneous dispersion of dye molecules and a better control of the loading. The covalent bonding in both routes necessitates the presence of at least one alkoxy function in the dye molecule that through hydrolysis and condensation allows the sol-to-gel transition. It is usual to use organosilanes as coupling agents to condense them onto silanols or other Me–OH groups present on the material surface or to co-condense them with metal alkoxides during the network formation. In this latter case they also play a role of network former; a spacer group between the condensable group and the optically active part is also usually present. More recently other incorporation methods have been explored. One can cite the capillary electrophoresis doping technique which uses the transportation of molecules based on the electrophoresis phenomenon in liquid under an electric field.[9] A new synthetic concept has been developed to produce dye functionalized xerogels *via* a nucleophilic aromatic substitution of fluoro-aromatic compounds with aminosilanes.[10] This one-pot synthesis process combines sol–gel processing and nucleophilic aromatic substitution reaction and gives hybrid materials with covalent bonding between the organic and inorganic sides. Fluoro aromatic compounds with different reactivities for nucleophilic aromatic substitution reactions containing azo, azomethine and diphenylamine groups have been also used for fine tuning of the optical properties of the resulting chromophoric xerogel.

Most of the active hybrid sol–gel materials for optics are made from the incorporation of dye molecules which are dispersed in the host matrix. Interesting hybrid systems have been prepared by the growth of organic nanocrystals in the sol–gel matrix. The process based on confined nucleation and growth of dyes in the pores of dense gels leads to narrow size distributions of 10–20 nm diameter particles. This approach has been rapidly extended to thin film technology using the spin-coating deposition process. Optical properties such as luminescence, nonlinear optical properties and photochromism have been observed.[11,12] Another interesting approach has been developed by the group of D. Levy and consists in the dispersion of liquid crystal droplets within a sol–gel matrix[13] for electro-optical applications.

The optimization of the host matrix, in terms of structure and properties is of paramount importance and has been the focus of several studies. The design of the host matrix concerns not only the problem of incorporation of the optically active species, but also transparency, refractive index, dye photostability and long term durability, mechanical properties, adhesion, shape-modeling, preparation process, OH content, hydrophobic/hydrophilic character, mechanical properties, and adhesion properties. A fast sol–gel process to make transparent sol–gel matrices suitable for different optical applications such as waveguides and submicron structured plates has been recently reported.[14] The basis of this novel fast sol–gel process for hybrids is to complete the reaction of all precursors and to evacuate the residual products (alcohol and water) before gelation. The sol–gel reaction has been performed under varying pressure conditions (from several atmospheres down to vacuum). This fast sol–gel technique allows reproducible preparation of materials with well-controlled properties and the mechanical and optical properties of the fast sol–gel material can be custom designed by changing the molar ratio of the precursors. Moreover they can be cast as either bulk monoliths, thin films or as a bonding phase between glass components. In most of optical application domains, OH groups should not be present in the final material since they cause luminescence quenching effects, optical losses, and water adsorption. Different strategies have been developed to reduce or suppress OH groups; the most common are using a non-hydrolytic sol–gel processing and the introduction of highly reactive transition metal alkoxide inorganic precursors such as titanium or zirconium alkoxides.[15,16] We should in any case underline that almost endless possible combinations to develop hybrid materials are in principle available and very much case-by-case tailoring is the main strategy which is followed. For such materials, the main routes are co-condensation of organosilanes with traditional metal alkoxides, preparation of composites formed by an inorganic network and an organic polymer, polysesquioxane-based systems and inorganic nanoparticle dispersions within an organic polymeric matrix (or *vice versa*).

The optical field is one research domain where hybrid sol–gel materials have been largely studied.[5,7,17,18] The first researches were mainly based on dye-doped sol–gel inorganics and focused on the improvement of the photostability and/or the segregation of the organic chromophore. Since then, studies have progressed to more sophisticated systems where the matrix is properly designed to optimize dye properties at different stages of the material life and mainly under external factors. The sol–gel process has been also found to be a good method to develop multifunctional hybrid materials since different components may be mixed in the same material framework. Multicomponent systems have evolved from nano- to macroscale. At the nanoscale it concerns tailor-made host matrices in terms of optical and mechanical properties, adhesion, which possess properties provided by the different constituents or multi-chromophore incorporated systems for specific phenomena such as energy transfer. The macroscale concerns specific optical multilayer systems such as those developed for antireflective coatings. Nano- and micro-structuration, which can be self-induced of stimulated by external tools have been also applied for a long time. With the discovery of ordered mesostructured oxide based materials,[19] the nanostructuration induced *in situ* by the organic self-assembly templating route has been applied for developing optical hybrid sol–gels.[20,21] This approach was recently extended to the fabrication of nanopatterned hybrid surfaces for integrated optics.[22]

The applications of hybrid materials in optics range from "traditional" uses, such as decorative coatings to very sophisticated nanostructured hybrids for photonics. Examples of transparent coatings both for functional and decorative applications are: sol–gel decorative coatings on glass, mineral and metal surfaces, UV-curable glass protective coatings (commercialized by HSG), protective hard coatings for transparent plastics (Institut für Silicatforschung), abrasion and scratch resistant coatings for aircraft windows (Boeing), hard and transparent coatings for protection of glass optical fibers (which improve mechanical strength, water corrosion, mechanical and chemical damage, abrasion, high-temperature degradation), photochromic coatings for glasses; contact lenses; solid-state lasers and waveguides, insulating materials in the microelectronics industry, coating on glass, metallic or plastic surface against corrosion, and low refractive index coatings.

In the present review, three research areas have been mainly considered: passive and active optical hybrid sol–gel materials, and integrated optics; it is noteworthy that these research themes are not unilateral and can be followed jointly. In writing this review we have tried to give a general overview following a logical development of the subject with these three themes, some developments are not fully covered such as for metal and semiconductor hybrid materials or mesostructured hybrids, but the reader can refer to other reviews in the same volume or to recent literature.[18,23]

One final introductive note about the nomenclature of the materials that we have used in this review: in general we have avoided the use of commercial names, such as Ormosils, Ormocers or Hybrimer; their use is quite confused and often misleading for those not expert in the field, we have therefore always preferred the term organic–inorganic hybrid which appears more generally descriptive of this class of materials and more appropriate for an academic contest.

2. Passive optical hybrid sol–gel matrices

Hybrid materials in optics may be classified in two main types: passive and active optical organic–inorganic materials. In passive optical hybrids, transparency and refractive index are of importance, while active hybrid systems are obtained by incorporating in the inorganic or organic–inorganic matrix an organic, metallic or organometallic optically active moiety. Passive hybrid sol–gel materials have been widely studied for applications related to surface coatings and are particularly attractive for their high transparency, good adhesion, barrier effects, corrosion protection, easy tuning of the refractive index and adjustable mechanical properties.[24–27] Moreover, the large possibilities of doping and/or structuring these materials while keeping good optical transparency enlarge their application field to antibacterial, and colored coatings.[28–32] The most important property of glass is its luminous transmittance, which is the basis for applying plane glass in windows of buildings and vehicles, as front covers of displays and traffic signs. Glass is also highly accepted as a clean, impermeable and recyclable container material to distribute, store and consume beverages and other nutrition products. Modification of glass surfaces through sol–gel hybrid coatings is a successful example of industrial application of this material.

2.1 Hybrid sol–gel matrices with controlled refractive index

Optical properties such as transparency and refractive index strongly depend on both the structure and the composition of the coating. Concerning transparency, a particular attention must be given to the domain size and thus the compatibility of reactants in multicomponent hybrid materials. One advantage of sol–gel chemistry is the use of molecular alkoxy precursors which favor co-condensation if a mixture of precursors is used. In organic–inorganic hybrids usually made from organoalkoxysilane and Si, Al, Zr or Ti alkoxides, experimental conditions have to be controlled to favor co-condensation and avoid self-condensation of the hybrid network precursors. An easy control of the refractive index is usually obtained by using suitable network precursors and varying the composition. Depending on the targeted properties, the refractive index of the bulk hybrid material is often considered, and low or high values compared to silica glass ($n \sim 1.10$–1.46 depending on the OH content)[33,34] are required. Ti and Zr are generally preferred to reach high refractive index coatings. Pure organic species can also be applied as a refractive index modulator but their use is limited since the induced refractive index variations are quite low in comparison to metal oxide doping; hybrid sol–gel materials with high refractive index have been also obtained by incorporating phenyl groups.[35] Tunable refractive index has been performed by modulation of the concentration of phenyl groups;[36] a high refractive index over 1.52 can be reached by optimizing the matrix structure. Recently, an inorganic–organic hybrid resin has been prepared through sol–gel condensation and curing by a hydrosilylation reaction;[37,38] the combination of these chemical reactions results in a sol–gel derived organo-oligosiloxane-based hybrid material with substantially high thermal stability and refractive index. The fabricated phenyl based hybrid showed excellent optical transparency with high refractive index ($n = 1.56$). The transparency in the visible range has been maintained even after thermal aging at 200 °C in air for 1152 h. This high thermal stability at high temperature for long periods with high refractive index is a very good combination for use in light-emitting diode (LED) encapsulation. B. Meena *et al.* have judiciously used phenylsilsesquioxane and diphenylsiloxane precursors to form a polyphenylsiloxane hybrid matrix;[39] the obtained material has the interesting property to be soluble in any organic solvent without phase segregation making possible the choice and incorporation of dyes without miscibility problems. This strategy offers easy film preparation with high refractive index which opens tremendous possibilities for applications concerning the design of new optical and photonic materials.

Phenyl groups usually allow reaching refractive indexes comparable to systems which employ zirconium as refractive index modifier. Zirconium(IV) *n*-proproxide or diphenyldimethoxysilane have been used as both network former and refractive index modifier of an epoxy-functional hybrid sol–gel derived thin film system.[40] The comparative effects of Zr and phenyl content, and UV light on the optical properties of each material system have been investigated. Refractive index measurements have demonstrated that both refractive index modifiers have similar and comparable effects on the refractive index of the systems and could be used to tune them, within a certain range. Depending on the type of refractive index modifier and desired refractive index value, UV light could also be employed to modify the refractive index of the systems. However, since Zr catalyses the epoxy crosslinking reactions, the influence of UV light on the refractive index of that system becomes insignificant above certain Zr content.

Incorporation of metal alkoxides into polymers through the sol–gel process is of significant interest for tuning the refractive index of optical materials. Titania is commonly incorporated in silica based networks to get a high refractive index.[41]

Acetylacetone (AcAc) is usually used as chelating agent for titanium alkoxide precursors to control their reactivity toward hydrolysis; the influence on the refractive index due to the use of acetylacetone for the preparation of TiO_2 and SiO_2 based hybrids has been studied.[42] TiO_2–silica hybrid films, with and without AcAc, have been prepared to study the effect of the chelating agent on material properties. In absence of AcAc, the films showed higher optical transparency in the visible region; the refractive index of films increased from 1.54 to 1.64 at 633 nm with Ti molar fraction varying from 10 to 70%. Whereas, in the films containing AcAc, the refractive index has been found higher but inhomogeneous. A mixture of titania and zirconia has been introduced by mixing the corresponding alkoxide precursors with organoalkoxysilane as organic modifier to form a hybrid sol–gel coating with high and controllable refractive index for waveguiding.[43] Titanium dioxide has been chosen as an inorganic moiety for its high refractive index. However, the strong quenching effect and the high chemical reactivity of this metal alkoxide are negative aspects for waveguide fabrication (*vide infra*); the co-addition of zirconia in the precursor sol has allowed overcoming these problems.

High refractive index hybrid coatings have been also prepared by directly incorporating anatase titania nanocrystals into organosilica precursor sol.[44] The introduction of fluorinated species in hybrid films is also a way to adjust refractive index when low refractive indexes are required. In such approaches, the nature of the fluorinated species and fluor content influence the refractive index. A series of polyimide (PI)-fluorinated silicate nano-hybrid materials with low refractive indexes have been prepared by the sol–gel process; they are based on fluorinated-PI mixed with fluorinated organosiloxane network.[45] The refractive indexes of the hybrids can be controlled through the silica content or the fluorine content. Fluorinated inorganic–organic hybrid materials have been prepared from fluoroalkylsilane and methacryloxypropyltrimethoxysilane through a sol–gel process;[46] high fluorine content resulted in lower refractive index within a range which is closely dependent on the fluoro-alkyl chain length. Refractive index can be also modified by surface nanostructuration or creating a size controlled porosity to decrease the refractive index while keeping good transparency. Nanoporous films prepared by the sacrificial-porogen (pore generator) approach have been developed as antireflective coatings.[47] The nanoporous structures have been generated by removing organic sacrificial polymers from hybrid films of poly(methylsilsesquioxane) and organic polymer; the refractive index has been controlled by the porosity which on turn depends on the amount of organic polymer (% loading).

The control of the refractive index presents a high interest for coatings with antireflective properties. Antireflective coatings have been prepared from the polyvinyl butyral (PVB)/silica composite system.[48] Although no increase of the hydrophobicity has been observed with the introduction of 4% PVB, an excellent moisture resistance attributed to the absorption of PVB on the surface of AR coating has been characterized.

A bi-layer thin film stack that served as an antireflective coating has been developed with a low refractive index top layer made from a mixture of organosilanes and high refractive index bottom layer made from a mixture of titania and organosilane.[49] The reflectance and the antireflection coating have been controlled by adjusting the relative refractive indexes and the thicknesses of the top and bottom layers. Under optimized synthesis conditions, an antireflection coating has been obtained, exhibiting low reflection, 1% at 550 nm, in the visible range.

Multifunctional hybrid coatings with optical properties have attracted much attention since they combine different properties in one coating system. Recently a bi-layer device with antireflective, photocatalytic (self-cleaning), water repellent, and high water-wetting (anti fogging) properties has been prepared by sol–gel deposition of two successive oxide layers.[50] A methylated-silica coating with high transparency, high water resistance, close to zero water adsorption, and fairly high mechanical properties has been first deposited. An ultrathin crystalline TiO_2 nanoperforated layer was then deposited on top of the previous layer. This hard top layer acts as a protective barrier towards mechanical wear and assures high water wetting (anti fogging) and photocatalysis (self-cleaning) at the surface. Moreover, in such multicomponent systems, the thickness and the refractive index of this layer can control antireflectivity properties. Passive sol–gel materials can also play an important role in the development of electro-optic devices, because of their variety of available refractive indexes. They can be used for different applications such as passive waveguide transitions to minimize coupling loss or as cladding layers for the EO material[51] (*vide infra*).

2.2 Colored hybrid sol–gel materials

Transparent colored coatings have been rapidly developed for packaging purposes and have found commercially available applications;[52,53] intensive research in this area is still current. For most of the applications of dye colored coatings, the intensity and stability of the color are major issues. The color intensity depends mainly on the amount of dye in the coating matrix, however, when a large quantity of dye is introduced in the precursor solution, the dye molecules can aggregate to produce opaque and light dispersive colored coatings, whose optical quality is not appropriate for many applications. Thus, to get good quality intense colored coatings it is necessary to disperse a large amount of dye in the matrix avoiding molecule aggregation. Moreover, it has been found that the photostability of dye molecules depends on the properties of the inorganic matrix where they are embedded and on dye aggregation state. A ball milling of the starting solutions has been reported to be an effective process to produce a much better dye dispersion and thus obtaining more intense colors and more photostable dye colored silica coatings.[54] Colored hybrid coating processing is a relatively low cost method for modifying the glass with a sophisticated shape and high surface area. A composition based on aluminium tri-*sec*-butylate (TBA), phenyltrimethoxysilane (PhTMS) and 3-glycidoxypropyltrimethoxysilane (GPTMS) seems to be particularly suitable for these applications.[55] The incorporation of colored azo-dyes in boron–silica hybrid matrix has also been reported to form well colored films with good hydrophobic properties obtained with low amounts of chromophores.[56] It is noteworthy that in most of the cases the research concerns mixed systems where both passive optical properties such as transparency and refractive index and optical properties generated by the incorporated optical moieties are taken into account.

3. Optically active hybrid sol–gel matrices

3.1 Photochromic hybrid materials

Photochromism is an optical phenomenon discovered in the late 1880s[57,58] that can be described as a reversible change of color upon exposure to light. It results from the reversible transformation of a chemical species between two forms by the absorption of electromagnetic radiation, where the two forms have different absorption spectra. Photochromism can take place in both organic and inorganic compounds, and also in biological systems (for example retinal in the vision process). Photochromic materials have several important uses depending on the rates of the transformations; for example, fast transformations are required for optical switches, while slow transformations are useful for optical data storage media. Photochromic materials can also be used to form energy-conserving coatings, eye-protection glasses and privacy shields.

3.1.1 Photochromic hybrids for fast optical switches. The switching speed of photochromic dyes is highly sensitive to the rigidity of the environment around the dye. As a result, they switch most rapidly in solution and more slowly in a rigid environment such as a polymer lens. However, it has been reported that attaching flexible polymers with low glass transition temperature (for example siloxanes or poly(butyl acrylate)) to the dyes allows them to switch much more rapidly in a rigid lens.[59,60] Some spirooxazines with siloxane polymers attached switch at near solution-like speeds even though they are in a rigid lens matrix.

The strong interest found in the use of hybrid inorganic–organic sol–gel matrices to prepare optical photochromic devices is related to the numerous possibilities offered by this family of materials in terms of controllable matrix rigidity, dye–matrix interaction, high dye loading, and easy matrix shape modeling.[61] The advantages provided by the use of an inorganic–organic hybrid sol–gel glass hosting photochromic spirooxazin dyes compared to dye-in-solvent and dye-in polymer systems in terms of dye photochromic response and thermal stability was demonstrated rather early.[62] Most of the photochromic sol–gel hybrid materials with fast optical response have been made by embedding photochromic organic dyes such as spiropyrane and spirooxazine derivatives in hybrid silica-based sol–gel matrices (Fig. 1).[63–65] It was soon observed that the photochromic behavior of the dye is strongly dependent on the dye/dye and dye/matrix interaction.[66] The dye/dye interaction is usually controlled by the dye miscibility in the matrix, the dye loading and the incorporation method. When fast optical response is required, it was clearly shown that hybrid class I materials[5] where dyes are embedded with weak dye/matrix interactions are preferable. The grafting of the dye to the matrix backbone allowed increasing dye content without aggregation[67,68] but the strong dye/matrix interaction has been found to reduce the dye mobility and thus the thermal decoloration rate. In such systems, the spacer length between the dye and the matrix backbone could be varied to optimize the rate of photochromic reactions.[69] Grafting the dye to the matrix backbone has been also found to improve photochemical fatigue resistance and a more rigid matrix appears preferable in terms of photodegradation.[70] The nature of the environment surrounding the dye within the hybrid host matrix has a strong effect on its photochromic response. The adjustment of the hydrophobic/hydrophilic balance within the matrix has been revealed to be of paramount importance for controlling the competition between direct and reverse photochromism and thus the kinetics of the photochromic response of spirooxazine and spiropyrane dyes embedded in hybrid silica matrices.[64] The host matrix is not only considered as the most favorable environment of the dye in terms of optical properties but also as the most thermally and photochemically stable environment in terms of the material lifetime. The design of the matrix has therefore been studied to elaborate photochromic materials with desired photochromic properties depending on the targeted applications.[71] The optical response of the dye can also be controlled by the introduction of additives.[72,73] As an example, the photofatigue resistance can be improved by the combination of two organic additives, methylimidazole and perfluoroalkylsiloxane.[72,73] The role of the additive is not only restricted to the photostability of the material but also acts on the photochromic response. Recently, bistability was attained in a photochromic spirooxazine embedded sol–gel hybrid coating by introducing a zinc salt, which is able to form a chelate with the photochromic molecule when irradiated, resulting in a drastic reduction of the thermal bleaching kinetics.[74]

Tailoring the host matrix was quickly revealed as fundamental for both photochemical response and photostability of the materials. An important work in the design of the host silica-based hybrid matrices have been realized by the group of D. Levy.[75] Different aspects have been considered such as pore surface properties to control the dye/matrix interaction,[76,77] the size of the pores which might contribute to steric hindrance of the dye molecule,[78] processing parameters that control photochromic properties of the material,[79] and role of organic groups in hybrid matrices.[80] Although the main targeted applications for reversible photochromic hybrid materials are optical switches related, the interest for these materials is also found in applied areas such as toys, cosmetics and clothing. Due to their easy shape-modeling, photochromic hybrid sol–gel silica materials have been recently used to prepare fast-response photochromic textile fibers where the host matrix is tailored to assure not only the expression of the photochromic properties of the embedded dye but also a good covering and adhesion on the fiber.[81] In this case, both adhesion and mechanical properties are very important since practical fibers have been strongly sought for a long time. The properties of the silica-based matrix can be optimized by introduction of specific moieties such as epoxy groups to enhance both washing and abrasion durability of the photochromic coating layer, moreover the optical response speed was slightly increased as well.[82]

Although the reported studies concern mainly hybrid photochromic materials which have been processed as supported thin films or coatings, interest in other shape modeling has also

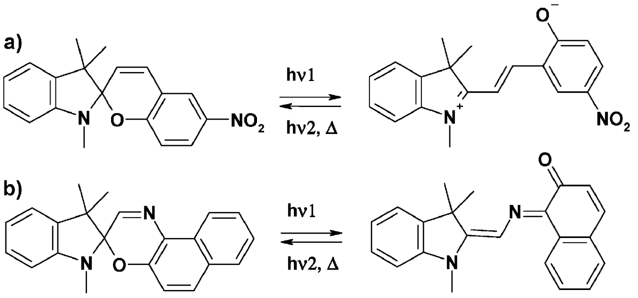

Fig. 1 Molecular structures of spiropyran (SP) and spirooxazine (SO).

been expressed. The synthesis of hybrid pigments by the incorporation of photochromic dyes (spirooxazine and spiropyrane derivatives) in surfactant templated mesostructured silica particles, and their subsequent incorporation in latexes to create solid films with relatively large, yet controllable, thickness has been recently reported.[83] The hybrid pigment provides a mechanical and chemically rigid framework that protects the dyes and facilitates handling.

The nanostructuration of the host matrix could be also advantageously used to improve hybrid material properties. An original strategy to increase colorability and mechanical properties of sol–gel photochromic film has been recently developed by impregnating a well-ordered 3-D hexagonal organosilicate mesoporous film with spirooxazine dye.[84] Fast photochromic response of spirooxazine and spiropyran dyes embedded in mesostructured silica materials was reported relatively early but the advantage of the mesostructured host was not clearly demonstrated.[85]

3.1.2 Photochromic hybrids for optical data storage.

Photochromic compounds such as diarylethene, dithienylethene and furylfugide derivatives (Fig. 2) have been incorporated in a hybrid sol–gel matrix because they exhibit an improvement of the photofatigue resistance and a better color stability. However, photochromism of these dyes and diazobenzene derivatives is based on a reversible isomerization which does not exhibit thermal fading at room temperature; therefore, a photochemically reversible change is observed upon alternating UV/visible exposition and thermal treatment. As these photochromic compounds are thermally stable and resistant to photochemical side reactions, they can be used in various applications such as switches and optical information storage.[86–89] An interesting phenomenon has been discovered with the use of diazobenzene dyes, which undergo a strong structural change during the photoisomerization (*cis–trans* isomerization) process (Fig. 3) which affects the medium around the molecules. Applications based on the photochromic behavior of diazo dyes have been proposed in the form of laser induced surface gratings.[90] The possibility to pattern thin azobenzene photochromic films at nanometer-size resolution has been demonstrated by Landraud and co-workers using aperture near-field optical techniques.[91] In particular it was shown that the matter migration induced by repeated photoisomerization cycles of the azobenzene dyes has created nanometer-size surface relief whose lateral size was defined by the tip aperture diameter and whose protusion height was directly proportional to the irradiation dose. These photoinduced properties were advantageously used to store information and to design optical devices (writing of channel waveguides and gratings).[92,93]

It was recently reported that azobenzene-containing TiO_2/silica-based hybrid films allow directly integrating the optical storage or optical switching devices with the waveguide devices on the same chip.[94a] Photoinduced effects on the host matrix upon isomerization of azobenzene dyes have been mostly studied, however, the influence of the matrix properties such as rigidity on both photoisomerization process and resulting bulk optical properties has been also investigated. In particular, the curing process of the as-prepared dye-embedded hybrid matrix has been found to be crucial on the dye molecules behavior and consequently on the birefringence, dichroism and transmittance properties.[94b]

Some organometallic compounds have photochromic properties and can be incorporated into sol–gel matrices for the preparation of optical hybrid devices. It has been demonstrated that nitrosyl complexes such as sodium nitroprussiate salt exhibit photochromic properties which are interesting for optical data storage applications. In this case the photochromic phenomenon is due to a reversible photoinduced structural change; upon irradiation, the conformation of the nitrosyl ligand switches to the isonitrosyl and a bent form. A photochromic ruthenium complex has been incorporated as nanocrystals within a sol–gel silica matrix.[94c] The photochromic properties are maintained in the composite with lower conversion rate due to the interaction of NO ligand of the complex and OH from silanol groups of the matrix.

3.1.3 Photochromic hybrids with inorganic chromophores.

The previous examples illustrate most of the research orientations and motivations in the development of photochromic materials based on the incorporation of organic photochromic dye within hybrid sol–gel matrices. Many inorganic substances also exhibit photochromic properties, often with much better resistance to fatigue than organic photochromics. Some studies on the development of hybrid photochromic materials using inorganic photochromic tungsten-containing compounds have been also carried even if on a much smaller scale. In most of the reported systems the inorganic photochromic component is used as the hybrid organic–inorganic network former.

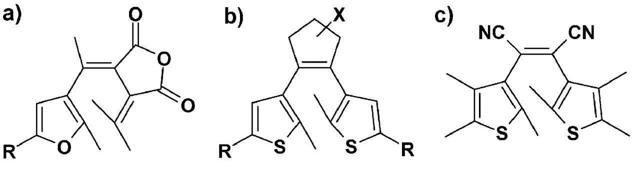

Fig. 2 Molecular structures of (a) diarylethene (DE), (b) dithienylethene (DT) and (c) furylfugide.

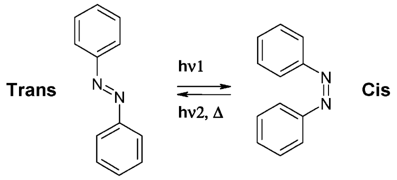

Fig. 3 *Cis–trans* photoisomerization of azobenzene.

However, only few examples have shown the possibility to embed the inorganic photochromic component as nanoparticles or nanoclusters within the hybrid silica-based matrix. The interest of photochromic hybrids with inorganic chromophores is mainly related to the easy shape modeling offered by this type of materials. An interesting strategy has been developed to prepare photochromic organosiloxane-based inorganic–organic hybrids by using tungstic acid to promote hydrolysis and subsequent condensation of 3-glycidoxypropyltrimethoxysilane.[95] It was demonstrated that the inorganic component derived from tungstic acid appeared to have Si–O–W bonds with the siloxane network. Tungstosilicate anions have been entrapped into the hybrid silica-based matrix with maintaining its Keggin structure.[96] The decoloration process related to the presence of O_2 occurs from the reduction of W^{6+} to W^{5+} due to ligand-to-metal charge transfer with simultaneous formation of a free radical; the resulting hybrid film exhibited excellent photochromism, mechanical strength and thermodynamical stability. Polyoxometallates (POM) have been embedded in hybrid silica films by covalent grafting through electrostatic encapsulation with hydroxyl-terminated surfactants.[97] The resulting functional hybrid film has both the transparent and easy processing properties of the silica matrix and the stable and reversible photochromism of POMs. Moreover, the redox properties of POMs have been advantageously used in these systems to realize the *in situ* synthesis of metal nanoparticles in the film. Transparent hybrid silane–WO_3 films have been prepared by mixing WO_3 nanoclusters and organosilane sols.[98] The coloration process has been found to be due to the formation of W–O–H structures that unfortunately lead to a very slow bleaching process.

3.2 Hybrid solid-state laser-dye materials

Laser dyes have been used for many years as a versatile source of tunable coherent optical radiation and are commonly used both in lasers and in optically pumped amplifiers. However, most of the dye lasers are solvent based and require pumping of the dye solution through a resonator to slow down photodecomposition. Therefore, there has long been an interest in fabricating solid-state gain media containing organic laser dyes because they provide ease of use and replacement. Moreover, the encapsulation of the dye in a solid matrix is favorable for decreasing health and environmental hazards.

Avnir and co-workers[4,99] first synthesized luminescent dye-doped sol–gel matrices and demonstrated the possibility of using them as solid-state dye lasers. However, only after a few years were the first laser emissions in sol–gel materials reported.[100–103] The main reasons for this delay are due to the several drastic conditions required to prepare efficient solid-state organic dye lasers. The laser material must exhibit an excellent transparency without scattering and a well-polished surface (surface roughness smaller than few nanometers). Other important parameters related to the laser emission are slope efficiency, output-energy pumping, lifetime and stability to aging. As a consequence of these several requirements most of the studies in this area have been focused on the tailoring of the dye/matrix system and the demonstration of laser emission. Different types of sol–gel matrices have been used as laser dye hosts such as silica or alumina xerogels, hybrid sol–gel materials and composite silica glass/polymer. Silica based hybrids that are class II hybrid materials have been quickly found to be good for constructing such solid-state dye lasers.[7,104,105] Indeed, the organic component could improve matrix characteristics such as hydrophobicity (to repel any residual polar solvent and thus protect the organic dye from chemical degradation), density (to decrease optical in homogeneities) and mechanical resistance (necessary to stand the surface polishing). It has been observed that hybrid laser materials exhibit substantially longer lifetimes and operate at much higher repetition rates than either inorganic xerogel systems or organic polymer hosts. These hybrid materials are able to provide a local environment to retain the strong fluorescent quantum yield of the dye and improve its photostability. Moreover, a high dye loading can be achieved with minimized dye aggregation when the active molecule is covalently anchored to the matrix backbone.[106] The development of a controlled hydrolysis process of hybrid precursors has allowed the synthesis of very dense and chemically stable matrices. The resulting materials exhibit a total absence of scattering losses all through the visible spectrum that clearly indicates the dramatic diminution of large pores. This not only affects the optical transparency of the laser material but also impacts its

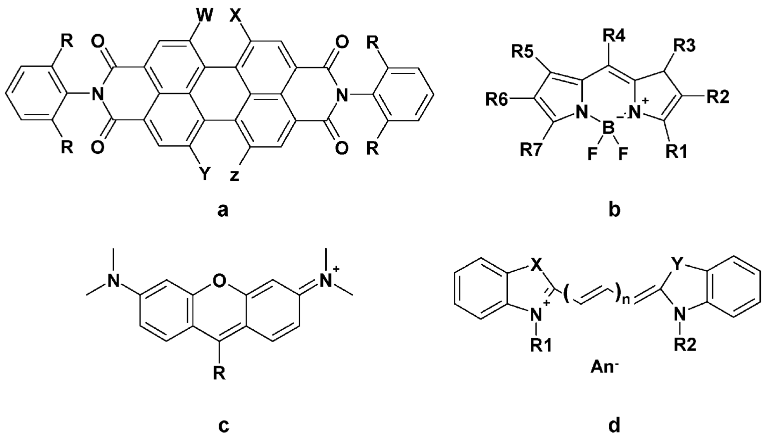

Fig. 4 Generic structures of (a) perylimide, (b) pyrromethene, (c) xanthene and (d) cyanine dyes.

thermal conductivity and therefore the thermal problems that arise when dissipating heat internally through optical excitation. Composite silica glass/polymers that are formed by two phase domains have shown good compatibility for dye and allowed a high dye loading. Moreover such structures allow combining the excellent thermal properties of inorganic glasses (higher thermal stability, lower thermal expansion and better thermal coefficient of refractive index) with the benefits provided by polymers (good compatibility with organic dyes, optical homogeneity and wide possibilities of modification of structural and chemical composition).

Performance of solid-state dye laser materials is not only based on the properties of the host matrix but also on the choice of the organic dye. The dye must be selected for appropriate spectral properties to match the desired lasing wavelength. It must be compatible with solid-state hosts, exhibit a good laser gain and be chemically, photochemically and thermally stable under the conditions of use of the laser. It is noteworthy, that the choice of dye for the gain medium is much more sensitive to photostability than is the case for liquid-solution dye lasers, because the dye does not flow and cannot be replaced after photobleaching. Different perylimide, pyrromethene, xanthene and cyanine dyes (Fig. 4) have lased in a variety of matrices including pure inorganic, sol–gel composites and hybrid matrices.[100,104,107–111] Perylene orange and related perylimide dyes have been the first dyes to be incorporated into sol–gel hosts[112–114] and have been found to be relatively photostable but less efficient as compared to other dyes. Although pyrromethene dyes are efficient, they are less photostable than perylimide dyes. Much effort has been invested in improving the longevity of pyrromethene-based solid-state dye lasers,[115] particularly by removing oxygen from the immediate environment of the dye. The xanthenes dyes relate to the rhodamine family for which the most common, rhodamine 6G, has been found to be an efficient and stable dye.[116] The cyanine dye family spans a very large range of wavelengths from green to infra-red. In general the longer wavelength cyanine dyes are less stable than their shorter wavelength relatives. Infra-red dyes, which belong to the cyanine family, have been used to prepare dye-laser materials,[117–120] not only to extend the wavelength covered by the sol–gel laser, but also relate to the possibility of developing a compact laser system that uses a diode laser as a pump. The synthesis of IR dye-doped sol–gel materials has received relatively little attention because of the low stability of cyanine dyes. Dunn and co-workers[118] reported laser action of 1,1′,3,3,3′,3′-hexamethylindotricarbocyanine (HITC) and other IR dyes embedded in hybrid matrices and thus provided evidence that sol–gel lasers can be fabricated throughout the visible spectrum and into the near infrared.

The huge optimization potential of hybrid solid-state dye-laser materials is illustrated by the strong improvement of their performance over recent years. The slope efficiency has increased from a few percent to more than 80% and the maximum output energies increased simultaneously from a few μJ to a few mJ. At the same time, lifetimes progressed from about 10^4 pulses in the μJ range to more than 10^6 pulses in the mJ range.[103] These results are very promising and it may be forecast that in the near future effective tunable solid-state dye lasers can replace liquid dye laser systems in certain applications.

The development of sol–gel/dye lasers, including the sol–gel technology, dye properties, and laser operation has been recently reviewed.[121] It has been emphasized that characterization of the host and the host/dye system is necessary for continued development of these systems. For this reason, methods based on the laser scanning confocal microscope have been developed to allow for small areas of the host/dye combination to be probed.[122] It is clear that optimization of the host matrix, that implies control of the synthesis parameters, is paramount for improving the laser action of incorporated dye. For this aim, a systematic study on the laser action of dyes doped into monolithic hybrid matrices with the synthetic protocols of the final materials prepared *via* sol–gel process has been realized.[123] The influence of both hydrolysis time, increased in a controlled way, and the nature of the neutralization agent on the laser action of pyrromethene 567, incorporated into hybrid matrices based on copolymers of methacrylate and 2-hydroxyethyl methacrylate with methyltriethoxysilane at the same time to be anchored to the inorganic network, have been studied. Both, enhancing the inorganic–organic compatibility through the matrix interphase, and the use of hydrolysis times smaller than 10 min, have been found to increase significantly the lasing efficiency and photostability of dye. The above conclusion can be generalized to optimize the synthesis of organic–inorganic hybrid materials with optoelectronic innovative applications independently of their composition.

The influence of several parameters on the lasing efficiency of hybrid sol–gel laser materials has been also investigated. Some comparative studies have been realized on the role of the incorporation of rhodamine 6G laser dye.[124] The photobleaching feature and photoluminescence properties are sensitive to the surrounding of dyes incorporated within porous sol–gel glass matrices and class II materials, where dyes are covalently bonded to the matrix backbone, exhibit improved performance compared to the class I materials where interaction between the dye and matrix backbone are weak. The time stability of the laser action of pyrromethene 605 dye-doped hybrid xerogels has been checked on several-year-old samples compared to fresh ones.[125] The porosity of the host matrix has since been found to control the light transport mean free path, thus optimization of the matrix microstructure is important.[126] Polymers have been used to create porosity by spinodal decomposition with a controlled porosity varying from microns to less than 100 nm.

An interesting approach for improving lasing properties is based on the use of a binary mixture of pyromethene dyes for doping hybrid sol–gel matrices;[127] the laser efficiency has been found to be improved up to 65% by using this co-doping route. Moreover, the tunabilities of these dye-mixed lasers have been extended to a large frequency region up to 70 nm. The incorporation of a binary mixture of laser dyes such as rhodamine 6G and perylene red within a hybrid sol–gel matrix has been also realized to generate energy transfer from rhodamine 6G donor to perylene red acceptor.[128,129] It has been demonstrated that the energy transfer depends on both the dye concentration and the dye ratio.

An interest in the development of hybrid materials with amplified spontaneous emission (ASE), which is a type of mirrorless lasing where spontaneously emitted photons are amplified by stimulated emission as they travel through a gain medium,[130] has been also emerged in recent years. These studies constitute a step towards device realization for integrated optical circuits. Yang and co-workers[131] showed the fabrication of mesostructured waveguides doped with the laser dye rhodamine 6G on low-refractive index mesoporous silica claddings. The waveguides exhibited ASE with a low pumping threshold of 10 kW cm^{-2} (instead of 200 kW cm^{-2} in silica sol–gel glasses for the same dye concentration) attributed to the mesostructure ability to prevent aggregation of the dye molecules. ASE has been also observed with a waveguide configuration based on a conjugated polymer blended with a zirconium-organosilicon glassy matrix.[132]

Pyrromethene and rhodamine dyes have been embedded in a composite silica glass/polymer matrix.[133] Lasing characteristics such as ASE efficiency, output peak wavelengths, output energies, and gains were found to be dependent on the dye concentration.

The preparation of sol–gel derived zirconia–silica hybrid films doped with near-infrared IR26 dye in order to obtain a solid-state dye laser material, which is promising for future distributed feedback (DFB) operation, has been reported.[134] Concerning the actual use in integrated optics, organic–inorganic hybrid planar and channel thin film waveguides obtained by sol–gel processes have been preferred to bulk materials, due to versatility and compatibility to DFB configurations. Waveguiding based on silica composites as optically active layer is restricted by the use of a support layer ultralow refractive index. A new synthetic approach for high refractive index, dye activated, hybrid mesostructured materials utilizing a fluorocarbon-stabilized titania precursor has been developed.[135] These solid and optically transparent titania composites have all the desired properties of their silica analogues, including nanoscopic domain separation and ease of patterning of the precursor solution, with the important added advantage of a higher refractive index, making possible planar waveguiding *via* one-step deposition onto simple glass substrates. The waveguiding ability of the hybrid titania mesostructured films can be used for mirrorless lasing applications such as ASE. Organic–inorganic sol–gel composites incorporating semiconductor nanocrystals have also attracted attention for optical gain applications. A composite polymer-sol–gel matrix was found suitable to stabilize quantum dots and quantum rods.[136] The excellent optical quality and waveguiding efficiency of the matrix provides optical gain in lower nanocrystal densities than needed in close-packed films. It also leads to improved optical gain performance manifested by prolonged stable ASE and reduced threshold pump powers. The sol–gel composite film shows a broadened temperature range of optical gain operation and a pronounced decrease in thermal and chemical degradation in comparison to a close-packed film.

Although most of the works concern hybrid sol–gel solid-state laser materials processed as transparent monoliths or films, recently a random laser emission was also obtained from dye-doped silica gel processed as powder.[137]

Hybrid organic–inorganic lasers are still one of the simplest continuously tunable lasers, and they remain an area of active study. First studies have been focused on the preparation of dye-embedded sol–gel matrices and improvement of lasing properties of the bulk materials. Several parameters, including dye choice and design, dye/matrix interactions, host matrix design, and experimental conditions, have been identified and optimized for improving laser efficiency. It is an area where the large potential offered by the sol–gel chemistry to design tailor-made hybrid systems has been widely demonstrated. Up to now, the performances of solid-sate dye lasers emitting in the visible region has been greatly improved, which allows solid-sate dye lasers to be commercially available. Solid-state lasers using infrared, blue[138] and UV dyes have also received attention but in minor proportion since the involved dyes exhibit more photostability problems to solve; nevertheless it is expected that they will rapidly reach the same development level. For the last decade, researches in this field have been involved in the development of solid-state laser dyes systems compatible with wave guiding technologies for application in integrated optics.

4. Hybrid materials for integrated photonics

One of the most successful developments of sol–gel hybrid materials is the fabrication of photonics devices for optoelectronics;[139] a large variety of applications has been envisaged in this field and several products are now on the market. An advantage of sol–gel hybrids for optoelectronics is the high versatility of the material processing, which allows preparing waveguides and photonic devices by different methods and low-cost technologies.[140] A clear advantage is the flexibility of the chemical synthesis, the low temperature bottom-up route and the potential better properties in comparison to the main competitor materials such as inorganic oxides and organic polymers.[141] Application in "integrated photonics" of hybrid materials for fabrication of different optical components, such as waveguides, beam splitters, gratings, couplers has been definitely demonstrated.[142] In this section we will briefly describe some of the applications in optoelectronics that have been developed so far using hybrid materials.

4.1 Planar and channel waveguides

Planar and channel waveguides for integrated photonics must have low optical losses at the telecommunication wavelengths in the near infrared region, specifically at 1320 and 1550 nm. In planar waveguides, which are in the form of film on a planar substrate, the light is free to propagate in all the in plane directions while in channel waveguides the light is further confined within the strict geometry of the channel. Hybrid and sol–gel films typically report optical losses lower than 1 dB cm^{-1}, which are intrinsically much higher than optical fibers (ultra-low losses fibers have optical losses lower than 1 dB km^{-1} at 1550 nm);[143] integrated photonics devices are, however, generally designed to have small dimensions, typically no more than few cm, and optical losses between 0.1 and 0.5 dB cm^{-1} are acceptable. Optical losses of hybrid materials in the near infrared range depend very much on the absorption of OH and C–H groups around the

Table 1 A comparative qualitative evaluation of the advantages *vs.* disadvantages of using hybrid materials for integrated optics as an alternative to pure inorganic oxides from sol–gel processing

Hybrid waveguides	Inorganic oxide waveguides
Thermal stability up to 300 °C	High temperature thermal stability
Low temperature processing	High temperature processing
Amorphous structure	Crystallization upon annealing
Easy patterning by different lithographic technologies	Smaller number of lithographic technologies can be used
Large thickness per single layer, high aspect ratio achievable	Small thickness per single layer (<500 nm)
“Flexible” layers can be obtained	“Rigid” fragile layers
No or low residual stress in the films	Residual stress in thin films
Good planarization properties, no treatment necessary	Medium planarization property
Deposition on flexible substrates is possible	Only rigid planar substrates

telecommunication windows. Strategies to overcome these problems are based on reduction of OH content developing specific synthesis routes or on changing the material composition to reduce the optical absorption due to organic groups; substitution of C–H with fluorinated groups is one of the most common strategies. On the other hand an intrinsic advantage of hybrid materials for planar waveguides is that scattering losses due to the surface roughness are low and no planarization treatments are necessary, such as in the case of other oxide materials.[144] Some of the advantages of hybrid materials for fabricating planar waveguides in comparison to sol–gel oxide films are summarized in Table 1.

The chemistry that has been developed for the fabrication of waveguides is relatively simple; the two most popular organically modified alkoxides which are used for fabricating photonics components contain polymerizable methacrylate or epoxy groups, such as 3-methacryloxypropyltrimethoxysilane (MPTMS) and 3-glycidoxypropyltrimethoxysilane (GPTMS).[145] The hybrid materials obtained from these alkoxides can be easily photopolymerized[146] by adding a photoinitiator in the precursor sol. Epoxy groups are more “sloppy” to open in comparison with methacrylate but the final material has generally better properties in term of mechanical[147] and chemical durability. On the other hand the chemistry of GPTMS is quite complex because several side reactions during sol–gel synthesis can be observed and fine design of the material is, therefore, quite difficult.[148,149] The refractive index is tuned by adding a transition metal alkoxide which can also be used as catalyst for epoxy opening; the drawback of this synthesis is that chelating agents,[150] which can be a source of impurities such as additional residual carbon after thermal processing of the material, are generally employed to reduce the high hydrolytic reactivity of these alkoxides.[151] The two chemical reactions that are involved, which are the polycondensation of inorganic groups and polymerization of organic functions are in competition; if the inorganic network formation is too fast there is not enough room for the formation of extended organic chains.[152] The hybrid structure which results, therefore, is affected by the synthesis protocol even if the composition of the material does not change. In general, the complexity of the chemistry is quite overlooked in the scientific literature, even if the overall material properties are very dependent on only small changes in the chemical synthesis.

Another important requirement for waveguide materials is reducing the amount of silanols,[13] also in this case several strategies, which witness the high versatility of the hybrid chemistry, have been proposed. An interesting example is the co-condensation of diphenylsilanediol (DPS) with MPTMS which is used to prepare hybrid films for planar waveguides that show surprisingly low optical losses (0.5 dB cm^{-1}) in the near infrared even if they are not fluorinated,[153] high aspect ratio hybrid films can be also fabricated.[154,155] Diphenylsilanediol has been co-condensed with different alkoxides containing polymerizable functional groups, such as MPTMS,[156] GPTMS[157] and vinyltriispropenoxysilane (VTIPS);[158] the steric hindrance of phenyl groups in DPS in general avoids self-condensation reactions and favours alkoxylation. An example of this reaction is shown in Fig. 5; DPS reacts in non-hydrolytic conditions with VTIPS and acetone is formed as a byproduct which is immediately eliminated by evaporation.

It is important to stress that an intrinsic advantage of using hybrid materials for applications in integrated optics relies on the possibility to apply a large variety of lithographic technologies and that even direct writing, without using any photocatalyst, by use of intense sources of X-rays is possible. Several types of channel waveguides and splitters, have been prepared; waveguide Y splitters with different opening angles, low propagation losses and good splitting effect have been fabricated.[159–161]

Hybrid materials for optical waveguides show, in general, good adhesion on different substrates and this property allows fabricating flexible waveguides on polymeric substrates. A non-hydrolytic sol–gel synthesis using 3-acryloxypropyltrimethoxysilane and 4-4′-(hexafluoroisopropylidene)diphenol

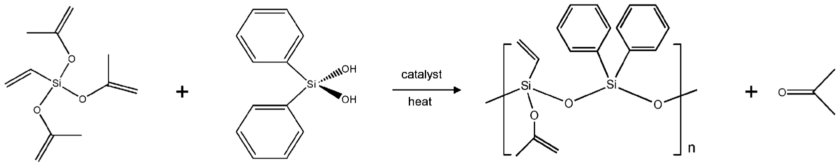

Fig. 5 Condensation reaction of diphenylsilanediol with 3-methacryloxypropyltrimethoxysilane.

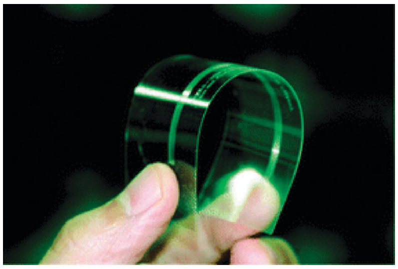

Fig. 6 Hybrid organic–inorganic optical waveguide deposited on a flexible substrate. Reproduced from ref. 162 with the permission of the Royal Chemical Society.

has been used to obtain a flexible waveguide array with no significant bending losses above 2 mm diameter curvature.[162] Fig. 6 shows one example of such type of optical waveguides on flexible substrates (from ref. 162).

Fabrication of hybrid organic–inorganic waveguides and lithographic technologies. Planar waveguides are obtained by deposition of a coating layer on a substrate of lower refractive index, the third low refractive index medium is generally air but a capping layer can be also used to cover the guiding layer. The light is entrapped within the high refractive index layer and propagates in any direction parallel to the substrate. It has to be underlined that hybrid materials can be used not only for the guiding layers but also for the buffer and capping parts of the device, or can be separately integrated in different systems, which means only one of the layers is used for fabrication of photonic systems based on different types of materials, such as organic polymers or inorganic oxides. An example is the hybrid film obtained by reaction of MPTMS and 3,3,3-trifluoropropyltrimethoxysilane which is commercialized as a cladding layer.[153] Optical circuits require, however, the fabrication of 3D optical channel waveguides and in this case application of lithographic technologies is necessary. The advantage of hybrid materials is that a large variety of lithographies from hard (X-rays) to soft (soft-molding) can be applied. The most common is UV lithography,[154,163,164] which is a simple, low cost, widely available and quite reliable fabrication method; other examples are soft-lithography,[158] rapid ion etching (RIE),[165] electron beam lithography (EBL),[166,167] femtosecond laser-based writing,[168] deep X-ray lithography (DXRL)[169–171] and soft X-ray lithography.[166] An example of microstructures obtained *via* soft-lithography is shown in Fig. 7; the microstructures are obtained by pressing a polydimethylsiloxane mold on the hybrid material layer which appears well suitable for the application of the "soft" lithographic writing techniques.[158]

The UV lithography of hybrid materials is based on photopolymerization of the methacrylate or epoxy through activation of the photoinitiator.[172] The UV light decomposes the photoinitiator into free radicals that open the methacrylate double bonds or the epoxy rings. This process induces an organic polymerization with formation of chains whose length, as we have previously underlined, depends on several synthesis and processing parameters, such as for instance the aging of the sol or the pH of the precursor sol.[152] The unexposed area is then etched to leave the patterned film; in this specific case the hybrid material acts as a negative tone resist upon exposition to UV light.

The effect of X-rays on hybrid materials has been recently used to develop direct patterning lithographies; the advantages of these techniques is that no photoinitiators are necessary to activate the polymerization and hybrid materials behave as negative resists upon exposure to X-rays. Both soft X-rays (typically in the 1–4 keV range of photon energy) and hard X-rays (DXRL) (5–25 keV of photon energy) have been used. In particular, the advantage of opening the epoxy by soft X-rays is clear, which is more difficult to achieve *via* UV photopolymerization. Fig. 8 shows the patterned structure obtained after chemical etching of a hybrid silica film

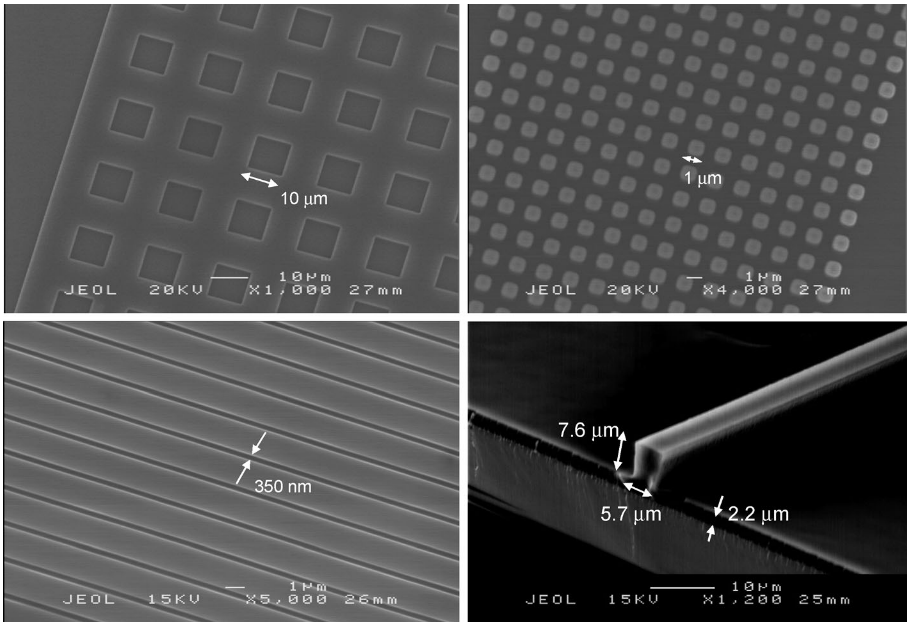

Fig. 7 SEM images of microstructures obtained on hybrid coating layers by soft-lithography (images courtesy of Prof. Masahide Takahashi).

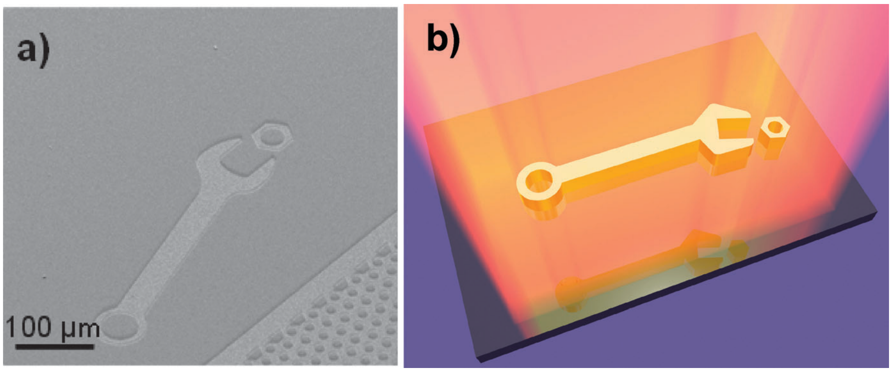

Fig. 8 Electronic image taken by SEM of a patterned MTES-TEOS film after chemical etching (a); the direct exposure to intense sources of X-ray (Deep X-ray Lithography) allows removing of the organic molecules and easy etching of the unexposed areas (sketch in b).

containing methyl groups (Fig. 8a); the film is directly exposed to high energy doses by DXRL that remove the organic molecules from the material and allow chemical etching of the unexposed side (Fig. 8b).

Alternative lithographic etching-free processes are currently under development; in general controlled wrinkling and corrugation of the hybrid film surface induced by selective exposure to UV light can be potentially an innovative low-cost and direct technology for fabrication of optics elements that are quite difficult or expensive to obtain by conventional lithographies. Several examples have been reported in literature, such as photolocking of volatile higher refractive index species in hybrid films, which is an extension to hybrid materials of a method which has been originally applied to organic polymers. Photoinitiators, such as benzyldimethylketal ($C_6H_5COC(OCH_3)_2C_6H_5$] and 1-hydroxycyclohexyl phenyl ketone ($HOC_6H_{11}COC_6H_5$) have been used for the photolocking process. Photopolymerization is induced by excitation of the photoinitiator by UV light in the exposed areas of the film; after this step the volatile molecules are finally removed by a thermal treatment.[173] Another strategy to obtain self-ordered patterns is the formation of wrinkled microstructures of long-range order/orientation through photopolymerization of hybrid films. The wrinkling process is controlled by slowing the evaporation of the solvents to obtain a wet and soft film even several hours after deposition; the faster polymerization of the film surface generates a buckling effect whose control allows creating of micropatterns in the films.[174] A periodic array of titania–polymer hybrid pillars has been fabricated by this photo-induced self organization process (Fig. 9).

There is clear trend in the field which shows that the fabrication techniques are moving forward from the micro- to the nano-scale lithography also in the case of hybrid materials; this is a necessary step for production of a next-generation of optical devices of higher integration and smaller dimensions. Recent examples have shown, for instance, that ultra high density patterns can be produced using hybrid materials with a UV nano-imprinting process. A silicon mold with nano patterns is used for nano-imprinting such as in soft lithography and this process is combined with UV lithography using photosensitive hybrid materials; nano-patterns with 35 nm size and 70 nm pitch have been produced.[175]

4.2 Thermo-optical devices

The "hybrid" nature of organic–inorganic materials is nicely exploited through the modulation of thermo-optical properties in optical waveguides. A fine tuning of the thermo-optics coefficient (TOC) can be, in fact, achieved by changing the relative composition of the organic and inorganic components. The TOC expresses the change of refractive index, n, as a function of temperature and it depends on polarization changes (Φ) and thermal expansion coefficient (β) of the material in accordance with the Prod'homme theory:[176]

$$\frac{\mathrm{d}n}{\mathrm{d}T} = \frac{(n^2-1)(n^2+2)}{6n}(\Phi - \beta)$$

TOC can be, therefore, either positive or negative, depending if the predominant term for a specific material is the polarization or thermal expansion. In inorganic materials TOC is positive because the polarization with temperature is the main term, while in polymers, such as polymethylmethacrylate (PMMA), is negative because the influence of the thermal expansion is larger than the polarization effect. In hybrid materials TOC values are negative, which indicates that thermal expansion is the predominant effect. The TOC values that have been measured in different hybrid waveguides are slightly larger than in PMMA (-1.1×10^{-4} K^{-1}) and in general are comparable with those of optical polymers. In hybrid silica films (TMOS-MPTMS) the TOC (measured at $\lambda = 633$ nm) is in the range of (-2.0 to -1.3) $\times 10^{-4}$ K^{-1}, as a function of relative composition;[177] in MPTES-zirconia coatings a TOC = -2.1×10^{-4} K^{-1} has been measured ($\lambda = 633$ nm)[159] and -2.0×10^{-4} K^{-1} in MPTES-diphenylsilanediol hybrids.[153] The possibility of using hybrid waveguides in integrated thermo-optic components has been demonstrated by fabricating a 2 × 2 Mach–Zehnder interferometric optical switch on a silicon wafer using a hybrid material with TOC = -1.44×10^{-4} K^{-1}. At the wavelength of 1055 nm, the switch response time has been measured to be less than 4.2 ms with 9.3 mW of switching power.[178]

4.3 Multimode interference couplers

Multimode interference (MMI) is used in photonics to fabricate different types of optical devices such as Mach–Zender switches, modulators and ring lasers. MMI is based on self-imaging

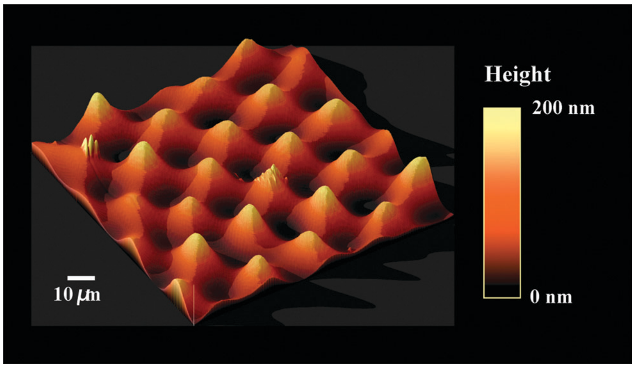

Fig. 9 A periodic array of titania hybrid pillars fabricated a photo-induced self-organization process.

which is the "property of multimode waveguides by which an input field profile is produced in single and multiple images at periodic intervals along the propagation direction of a waveguide".[179] An MMI device is generally designed to have single mode input channels (*N*) coupled to a central multimode waveguide and single-mode output channels (*M*); such type of devices are indicated as $N \times M$ MMI splitters. MMI devices based on hybrid materials have been fabricated by different groups; the easy processing and the low optical losses make organic–inorganic hybrids, in fact, very attractive for the production of this type of photonics devices. Hybrid photocurable films, based on MPTMS, are generally used; the refractive index is modulated by adjusting the composition and zirconium or aluminium alkoxides are used in the synthesis for this purpose. $N \times M$ MMI couplers of different geometries such as 1 × 2,[180,181] 1 × 3,[182] 1 × 4,[183] 1 × 8,[184] 1 × 12, 1 × 32 and 4 × 4[185] have been produced using different fabrication technologies. Fig. 10 shows the SEM image of a section of a MMI device (the core layer is a photocurable MPTMS-zirconia hybrid); multimode waveguide region (right side) and the output ports (left side) are shown (from ref. 182 with permission of IEEE).

More complex optical devices such as a wavelength division multiplexer (WDM) have been also obtained using hybrid materials.[186] A MMI-PHASAR (phase array) device working at 1550 nm, which is composed of a $N \times M$ MMI power splitter, an array of single *N* mode waveguides and a $N \times M$ MMI combiner has been prepared by UV lithography on a photocurable MPTMS-zirconia guiding layer.

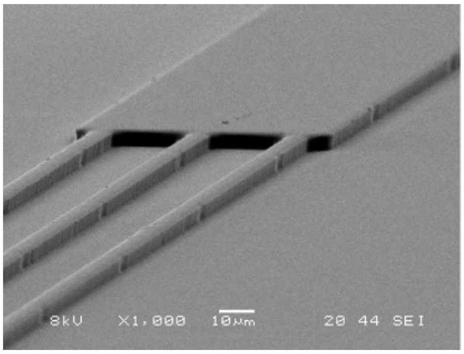

Fig. 10 SEM image of a section of a MMI device; multimode waveguide region (right side) and the output ports (left side) are shown (from ref. 182 with permission of IEEE).

4.4 Crystalline hybrid materials, birefringent materials

Hybrid materials are generally amorphous, and controlled crystallization with formation of hybrid crystals, is obtained only in very specific cases when bridged silsesquioxanes are employed for the synthesis. A very fascinating chemistry which uses bridged organically modified alkoxides for molecular recognition has been developed. An alkoxide which has a bridging organic spacer and a trifunctional silyl group at both the ends of the spacer[187–190] allows forming crystalline structures through self-organization. The organic units within the hybrid material self-organize through van der Waals interactions or hydrogen bonding[191] and different crystalline structures have been obtained, such as helical fibers or lamellar crystals.[192,193] Bridged alkoxides have been also used to obtain mesoporous organized materials with crystalline hybrid structure in the pore walls.[194] The possibility to obtain crystalline hybrids opens new perspectives in terms of functional properties and mechanical performances while thermal and chemical durability should be also highly improved. Crystalline hybrids as bulk materials have only limited applications in photonics but recently crystalline hybrid films with birifrangent properties have been obtained. Self-organization of hybrid crystals can be achieved, in fact, even using monofunctional organically modified alkoxides and without long alkyl chains.[195] Controlled aging of basic catalysed solventless sols of 3-glycidoxypropyltrimethoxysilane (GPTMS) allows the formation of crystals of some millimeters length through opening of the epoxy and formation of organosilica lamellar crystals in bulk materials. The process can be extended to obtain crystalline hybrid films through controlling the film processing conditions;[196] the crystalline films appear highly transparent: the formation of the self-organized nanocrystalline structures does not change the optical transparency of the material.[197] The amorphous hybrid film has isotropic optical properties whilst the nanocrystalline film exhibits optical anisotropy, $\Delta n = 1.88 \times 10^{-3}$, due to the orientation of the plate shaped crystallites. The hybrid crystalline films can be easily patterned through soft-lithography, square structures with excellent spatial resolution, as high as 350 nm, can be fabricated.

4.5 Planar optical waveguides for sensing

Planar waveguide chemical sensors have undergone a recent growing interest as an alternative to fibres and several devices have been fabricated based on planar waveguide technologies.[198] Hybrid materials have been also tested for chemical sensor platforms and some devices have been produced and tested as sensors for relative humidity,[199] ethanol[200] and isopropyl alcohol.[201] Different types of sensor devices have been fabricated, such as a planar waveguide ring resonator,[200] an optical MMI coupler[199] and a single-mode planar integrated optical waveguide.[201] A highly selective and sensitive method to detect trinitrotoluene (TNT) using molecularly imprinted polymer (MIP) films has been also used for developing an optical sensor.[202] A hybrid sensing layer is coupled with waveguide interferometry as a signal transduction platform. The sensing layers are hybrid organic–inorganic materials which include the covalent incorporation of a TNT analogue template during sol–gel reaction. After film processing, the template is removed by the cleavage of a carbamate linkage yielding a shape-selective binding site with the capability to recognize TNT.

4.6 Micro-optic elements

Sol–gel processing has been shown, in general, to be well adapted for fabrication of several types of micro-optic elements[203–205] such as diffraction gratings,[206] Fresnel lenses[207] and microlens arrays. Microlens arrays, in particular, are formed by multiple lenses which are aligned on a supporting substrate and are used in photonics for the optical interconnections between optical fibers and light-emitting or detecting devices. In general, microlens arrays are fabricated using organic polymers or oxide glasses but hybrid materials offer some distinctive advantages such as a potential higher thermal stability and an easier fabrication technology. Different examples have been reported in literature and some products, such as diffraction gratings are currently available in the market. Fabrication of microlens arrays is done using binary masks, with positive/negative tones given by unexposed/exposed areas or more commonly by grayscale photomasks. Photolithographic patterns of optical structures of modulated thicknesses can not be achieved in fact by binary photomasks, and grayscale masks which consist of zones of different optical density, have to be used. In the case of fabrication of a convex lenses by using a negative tone resist the grayscale photomask will have the highest transmission capability, *i.e.* the lowest optical density, in the centre of the lens which will gradually decrease from the centre to the edges. Several examples of fabrication of microlenses arrays using grayscale photomasks have been reported, using as photopolymerizable functional groups both methacrylates[208–210] or epoxides.[210,211] An example of cylindrical and spherical microlenses obtained using the epoxies in GPTMS as the organic polymerizable groups, is shown in Fig. 11.[167] Conventional proximity UV-lithography with a positive resist for large lenses, and nanoimprint lithography using stamps with a grating of ridges for small cylindrically-shaped lenses have been used. Alternative etching free techniques have been also applied for fabricating optical waveguides as well micro-optic elements by self-developing (*vide supra*);[212] a circular cone microlens array has been obtained using a less expensive binary photomask and a self-development method.[213]

4.7 Two-photon polymerization of hybrid materials for fabrication of 3D photonics structures

Two-photon photopolymerization (2PP) is a new method[214] that has been recently developed as a free-form fabrication process for production of sub-micron 3D solid structures.[215] The polymerization is initiated by an infrared laser with ultrashort pulses of the order of femtoseconds. The laser pulses promote the polymerization *via* two-photon absorption within the focused volume; the non-illuminated regions are then removed by chemical etching such as in the conventional UV lithographic process. 3D structures with a resolution of 100 nm can be fabricated by moving the laser focus through the material. 2PP has been applied to organic polymers, such as acrylate or epoxies but more recently also organic–inorganic hybrids have been used for fabricating complex 3D objects and photonic devices.[216] The two main problems to be faced for 2PP of hybrids is controlling the shrinkage upon polymerization[217,218] and increasing the refractive index of the material. Another basic issue is the control of the length of the polymerized organic chains, because the mechanical properties are strongly dependent on the network structure. In principle, the use of hybrid materials for 2PP can have the intrinsic advantage of better mechanical response and higher thermal stability with respect to purely organic materials. Some good solutions have been shown and 2PP has allowed

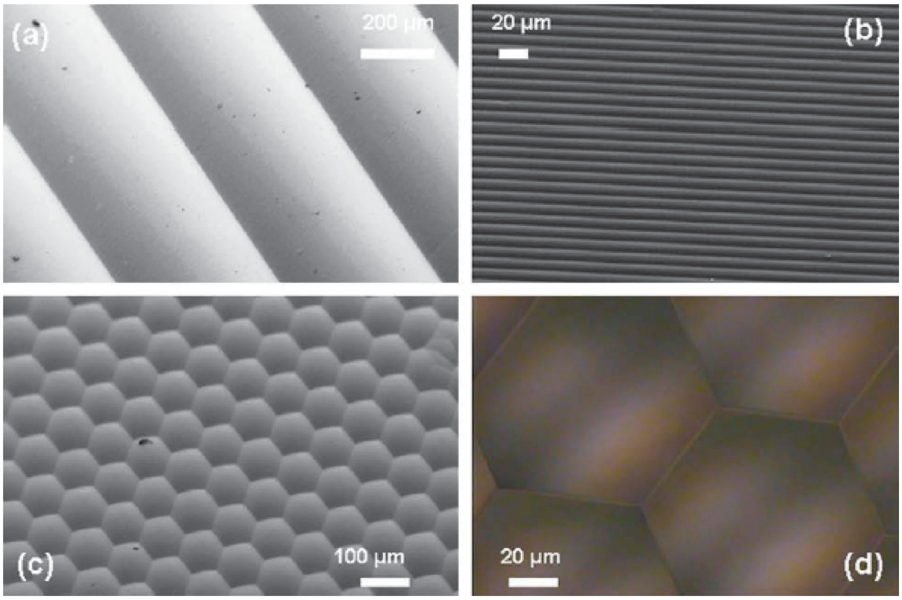

Fig. 11 SEM images of cylindrical microlenses with 400 (a) and 10 μm (b) of period. Triangular array of spherical lenses with 80 μm of period imaged by SEM (c) and optical microscopy (d) (from ref. 167 with permission of Elsevier).

fabricating hybrid photonics crystals,[219] microlenses[220] and optical waveguides.[221,222] In general, polymerizable methacrylate functions have been used for 2PP of hybrids, using MPTMS as the organically modified alkoxide; zirconium alkoxides have been added for increasing the refractive index,[223] while controlling of the processing conditions (laser intensity) is critical for avoiding excess of shrinkage in the material.[218] Different types of structures have been fabricated by 2PP of hybrids for other applications different from photonics, such as microneedles[224] and scaffolds for cell growth. 2PP has been also used to fabricate three-dimensional photonic crystal structures containing an active nonlinear optical chromophore, such as Disperse Red 1.[225]

An example of photonic crystal with a woodpile structure obtained by 2PP of a zirconia-MPTMS hybrid system is shown in Fig. 12 from ref. 223. An alternative route for 2PP of hybrids, which is based on controlled photopolymerization in porous materials, has been recently proposed. A porous hybrid host material has been impregnated by photopolymerizable monomers and waveguides have been fabricated by selective 2PP. It has to be observed that even if scientifically very attractive, 2PP is still not competitive as a 3D fabrication technique in comparison to other methods, such as stereolithography or digital light processing, because of the low writing speed and relatively low efficiency of the photoinitiators. In the case of optical waveguides, however, because only monodimensional lines have to be designed the 2PP process can become more competitive.

4.8 Hybrid materials for non-linear optics

An interesting field of application of hybrid materials is in non-linear optics for modulation, limiting and switching of optical signals. This is a fast moving field in which hybrid materials can play an important role for the development of the next generation of integrated devices which can include organic photonics.[226] Despite the promises of challenging organic polymers in the field, still hybrid materials appear to have a limited role in development of active layers, especially in non-linear optics[23,227] A clear trend is the employment of hybrid materials as passive components in integrated non-linear optical devices in which the organic polymers are used as the active layers. We have recently dedicated a specific review to this topic and we will present here, therefore, a shorter overview with the addition of the more recent findings.

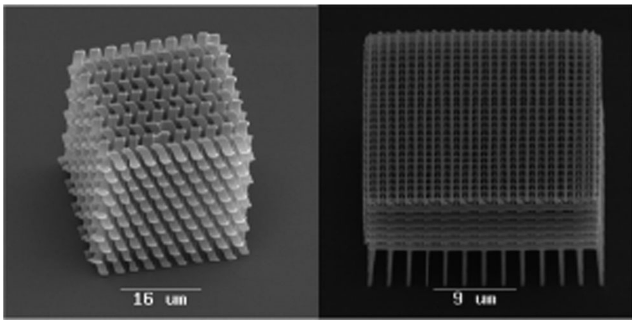

Fig. 12 3D photonic crystal structure fabricated by 2PP technique (reproduced with permission of the American Chemical Society from ref. 223).

4.8.1 Electro-optic hybrid organic–inorganic materials.

The preparation of hybrid materials for EO applications requires as first step the design and synthesis of NLO chromophores with high molecular hyperpolarizability which can be incorporated in a solid-state matrix *via* direct chemical bonding during sol–gel reactions; physical entrapment is another possible option, in this case the chromophore should exhibit a high solubility on the solvents used for sol–gel processing. Immediately after the film deposition the NLO chromophores are then poled to achieve a non-centrosymmetric orientation; an efficient orientation is very much depending on the nature of the matrix and its compatibility with the main poling processing technologies. In general, physical entrapment is simpler but has the disadvantage of a shorter temporal stability in terms of molecular alignment upon poling, and covalent bonding to the matrix is preferred. The efficiency of the electro-optics response depends on the polarizability of the chromophore, the loading amount and the possibility of orienting the molecule in the hybrid matrix. Another critical feature is the stability of the orientation after poling which for a working device is a highly demanding requirement. If the matrix of the NLO chromophore is an organic polymer, thermosetting materials that cross-link during thermally assisted poling are used to prevent NLO relaxation.[228] Optimized thermosetting materials have a T_g higher than 200 °C and maintain a large EO coefficient at high working temperatures. In the case of hybrid materials the design of the host matrix is complicated by the thermally induced condensation of the inorganic side; if condensation is too fast during thermal poling alignment of the chromophore will be hindered. The most widely used strategy for preparing hybrid materials for EO applications is functionalization of the NLO chromophore with alkoxy functions, for instance *via* reaction with a coupling alkoxide such as 3-isocyanatopropyltriethoxysilane, to get a covalent bonding directly to the matrix during sol–gel processing. The chromophore can be then co-reacted with TEOS or directly with an organically modified alkoxide; the choice is very much dependent on the nature of the chromophore and other requirements of the device, such as film thickness and mechanical properties. The synthesis of the hybrid matrix can be quite complicated by the nature of the NLO molecule that may require a finely designed matrix, such as in the case of zwitterionic chromophores (*vide infra*). The solubility of the chromophore in the precursor sol is also very important because the performances of the device depends on the dye loading.[229] Avoiding the formation of aggregates within the matrix and dipole–dipole interaction is also another problem to be addressed during material design. In general, literature data show that alignment of the chromophores in hybrid materials is not critical and order parameters,[230] Φ, up to around 0.35 have been reported.

The number of bonding sites and their geometry in the alkoxy-modified chromophores is another very interesting synthesis parameter that can be designed; chromophores with one, two or three grafting sites have been obtained.[231] Interestingly, it has been shown that chromophores with three bonding sites have a lowest capability of orientation[232] than dyes with two sites, while those with two bonding sites in the vertical positions with respect to the dye chain, have shown the highest alignment (ϕ = 0.31) and d_{33} value (Fig. 9). Several examples of alkoxy functionalized dyes which are based on different functional groups have been reported in literature so far; the main group comprises functionalized or modified azo dyes of the type of Disperse Red such as Disperse Red 1 (DR1),[233–235] Disperse Red 13,[236] Disperse Red 17,[237,238] Disperse Red 19,[239–241] and Disperse Orange.[242,243] Other alternative chromophores have been also synthesised for NLO development of hybrid materials, such as for instance organically modified alkoxides containing a thiophene ring (**1** in Fig. 13),[244] benzimidazol derivatives (**2** in Fig. 13),[245] azole heterocycles (**3** in Fig. 13),[246] and triphenylamino derivatives (**4** in Fig. 13).[247]

Dendrimer type hybrid materials have also been tested for EO applications; dendronized alkoxysilane dyes (Fig. 14) have been synthesised *via* the ring opening addition reaction of azetidine-2,4-dione of chromophore-containing dendrons, with 3-aminopropyltriethoxysilane. In a second step the dendronized modified alkoxide has been co-condensed with phenyltriethoxysilane (PTES) to obtain a hybrid material; an EO coefficient (r_{33}) of 2.9–13.0 pm V^{-1} has been measured with optical losses in the guiding layer from 3.2 to 4.2 dB cm^{-1} at λ = 1310 nm.[248]

An important alternative to this general class of chromophores are push–pull[249] zwitterionic dyes; they exhibit in polar solvent an aromatic and highly zwitterionic ground state and a quinoidal excited state, which is the opposite from other NLO chromophores. These zwitterionic dyes, however, are easily photodegraded under the combined action of oxygen and light, and furthermore they are sensitive to acidic environments. On the other hand they show a very high hyperpolarizability, among the highest reported in literature, and are therefore very attractive for applications in non-linear optics. A push–pull zwitterionic chromophore, 1-[*N*-(3-*N*^{9}-diethanolamino-propyl)pyrid-4-yl]-2-[5-dicyanomethanido)thien-2-yl]ethylene (BisOHPETCN) (Fig. 15), with the two bonding sites at the head of the main chain and high hyperpolarizability value, has been specifically designed for grafting to a hybrid matrix.[250] The BisOHPETCN degradation mechanism involves singlet oxygen; the presence of the intramolecular charge transfer band means that the chromophores absorb photons, allowing the excitation of molecular oxygen to singlet oxygen. It has been observed that the presence of the amine groups significantly reduces the photobleaching process. The hybrid materials has been, therefore, prepared by the co-hydrolysis of 3-aminoethylaminopropyltrimethoxysilane (AEAPTMS) and 3-glycidoxypropyltrimethoxysilane (GPTMS) which has allowed the incorporation of 15–20% by weight of these chromophores.[251] The presence of amine groups allow reducing the photobleaching degradation which involves singlet oxygen; a significant NLO response has been, however, observed only after co-doping the material with a physical spacer, (hydroxyethyl)carbazole, which confirms the importance of controlling the chromophore–chromophore interactions.[252] Second harmonic generation (SHG) measurements have given a d_{33} = 70 pm V^{-1}.

A recent trend is combining hybrid materials with organic polymers in fabrication of an integrated photonic device. In this case the hybrid materials are not used for the active guiding layer but for another part of the device. Using this approach hybrid materials have been also used to fabricate Mach–Zender and phase modulators[253] with in-device large electro-optic coefficients of 138 and 170 pm V^{-1}. These devices do not use directly the hybrid material for poling but are an interesting example of an integrated organic polymer hybrid material system for photonics applications[254] and the performances of these devices seem to challenge those of inorganic materials. The poled electro-optic material is an organic polymer containing AJC146 as dispersed guest chromophore; hybrid sol–gel materials are used for under cladding, core layer and over cladding. This approach seems to get the best benefits of some properties of hybrid materials, such as high conductivity at the poling temperature (135 °C), low dielectric constant and low dielectric losses at the working temperature (0–85 °C).

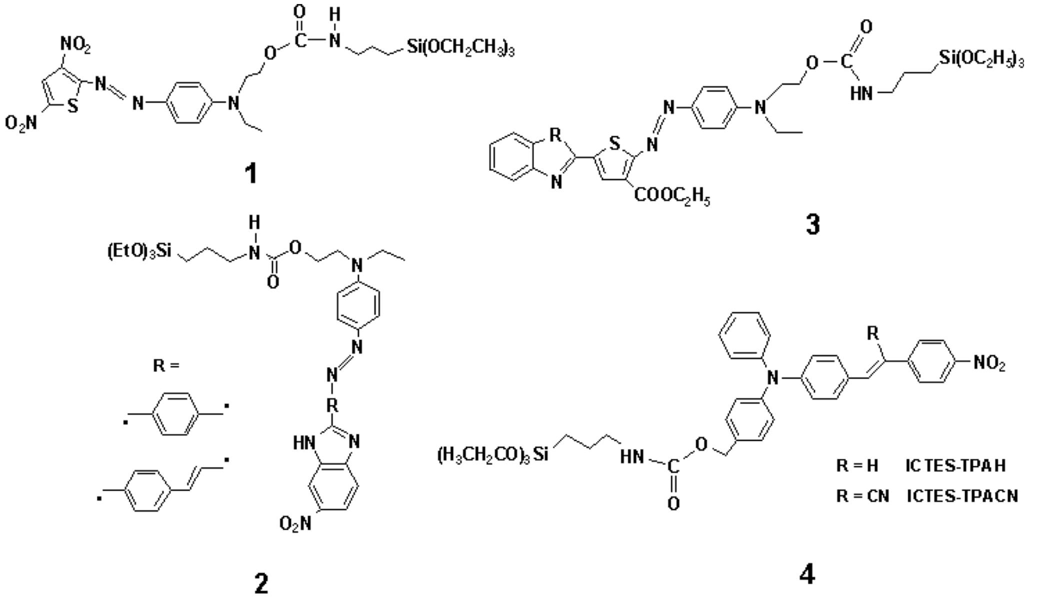

Fig. 13 Organically modified alkoxides with different chromophores for EO applications.

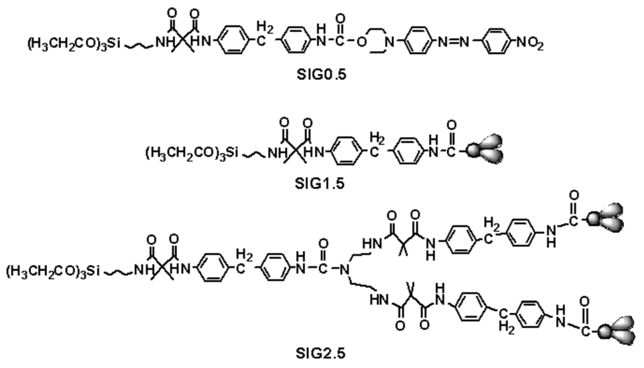

Fig. 14 Dendronized alkoxysilane dyes.

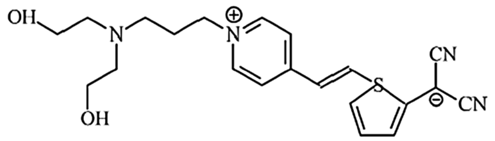

Fig. 15 The zwitterionic push–pull dye: 1-[*N*-(3-N^9-diethanolamino-propyl)pyrid-4-yl]-2-[5-dicyanomethanido)thien-2-yl]ethylene.

5. A future outlook

Hybrid materials for optics and photonics, as we have outlined in our review, have now reached a quite mature stage of development and several products are available on the market. In several applications, such as in integrated photonics they have, however, found only a partial success in challenging competing materials, such as organic polymers and purely inorganic materials. There are several reasons for this that are likely related to industrial politics, hybrid materials represent the last-comers in the field and several times it is difficult to replace well established technologies, especially in the coating industry, if the advantage is only incremental. Several properties of hybrids are somehow unique, such as the soft-chemistry flexibility that allows a very fine tuning of the material, but represent also a limit. Solvents, such as alcohols, are not easy to handle in industrial processes and clearly much research has to be devoted to "green" and alcohol-free processing of hybrids.

Integration of hybrid materials for optics and photonics into nanotechnology devices is also a clear trend; in this route we can easily forecast a bright future for nanohybrid materials. The possibility of integrating in one material several functions is not so easy to reach in comparison with other classes of materials. This step requires also the development of specific lithographic techniques that should move to the nanoscale and should be easily integrated in current industrial processes.

Finally we can also envisage a future where hybrid materials have nano-scale dependent properties but they are also able to self-evolve to complexity, this means auto-construction and self-assembly, environmental responsive smart materials and self-organization capability to build the final optical device.

Acknowledgements

Plinio Innocenzi and Benedicte Lebeau thank all the co-workers that have contributed to their work in this field in the past years.

References

1 J. Livage, M. Henry and C. Sanchez, *Prog. Solid State Chem.*, 1988, **18**, 259–341.
2 C. J. Brinker and G. W. Scherrer, in *Sol–Gel Science, The Physics and Chemistry of Sol–Gel Processing*, Publisher Academic Press, San Diego, CA, 1990.
3 H. Schmidt, A. Kaiser, H. Patzelt and H. Sholze, *J. Phys. Coll.*, 1982, **43**, 275–278.
4 D. Avnir, D. Levy and R. Reisfeld, *J. Phys. Chem.*, 1984, **88**, 5956–5959.
5 C. Sanchez and B. Lebeau, *Curr. Opin. Solid State Mater. Sci.*, 1999, **4**, 11–23.
6 C. Sanchez and F. Ribot, *New J. Chem.*, 1994, **18**, 1007–1047.
7 C. Sanchez and B. Lebeau, *Mater. Res. Bull.*, 2001, **5**, 377–387.
8 R. Reisfeld, *J. Fluoresc.*, 2002, **12**, 317–325.
9 J. Tagichi, T. Yano, H. Segewa and S. Shibata, *J. Ceram. Soc. Jpn.*, 2009, **117**, 1095–1100.
10 A. Seifert, K. Ladewig, P. Schoenherr, K. Hofmann, R. Lungwitz, I. Roth, A. Pohlers, W. Hoyer, G. Baumann, S. T. Schulze, M. Hietschold, N. Moszner, P. Burtscher and S. Spange, *J. Sol-Gel Sci. Technol.*, 2009, **53**, 328–341.
11 V. Monnier, E. Dubuisson, N. Sanz and A. Ibanez, *Res. Chem. Intermed.*, 2008, **34**, 155–167.
12 V. Monnier, N. Sanz, E. Botzung-Appert, M. Bacia and A. Ibanez, *J. Mater. Chem.*, 2006, **16**, 1401–1409.
13 M. Zayat and D. Levy, *J. Mater. Chem.*, 2005, **15**, 3769–3775.
14 R. Gvishi, *J. Sol-Gel Sci. Technol.*, 2009, **50**, 241–253.
15 C. Zha, X. Luo, R. Wang and B. Luther-Davies, *J. Mater. Sci.: Mater. Electron.*, 2007, **18**, 331–S334.
16 M. Oubaha, M. Smaihi, P. Etienne, P. Coudray and Y. Moreau, *J. Non-Cryst. Solids*, 2003, **318**(3), 305–313.
17 C. Sanchez, B. Lebeau, F. Chaput and J.-P. Boilot, *Adv. Mater.*, 2003, **15**, 1969–1994.
18 L. A. Dias Carlos, R. A. Sa Ferreira and V. de Zea Bermudez, in *Hybrid Materials*, ed. G. Kickelbick, Wiley-VCH, New York, 2007, pp. 337–400.
19 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710–712.
20 (*a*) C. E. Fowler, B. Lebeau and S. Mann, *Chem. Commun.*, 1998, 1825–1826; (*b*) B. Lebeau, C. E. Fowler, S. Mann, C. Farcet, B. Charleux and C. Sanchez, *J. Mater. Chem.*, 2000, **10**, 2105–2108.
21 B. J. Scott, G. Wirnsberger and G. D. Stucky, *Chem. Mater.*, 2001, **13**, 3140–3150.
22 A. Fisher, M. Kuemmel, M. Järn, M. Linden, C. Boissière, L. Nicole, C. Sanchez and D. Grosso, *Small*, 2006, **2**, 569–574.
23 P. Innocenzi and B. Lebeau, *J. Mater. Chem.*, 2005, **15**, 3821–3831.
24 C. Lim, I. S. Hong, S.-I. Hong, K. Jang, J. S. Kim and H. Kim, *J. Sol-Gel Sci. Technol.*, 2004, **30**, 117–128.
25 P. Belleville, C. Bonnin and J. J Priotton, *J. Sol-Gel Sci. Technol.*, 2000, **19**, 223–226.
26 E. Bescher, F. Piquè, D. Stulik and J. D. Mackenzie, *J. Sol-Gel Sci. Technol.*, 2000, **19**, 215–218.
27 G. Schottner, K. Rose and U. Posset, *J. Sol-Gel Sci. Technol.*, 2003, **27**, 71–79.
28 M. J. Saif, J. Anwar and A. Munawar, *Langmuir*, 2009, **25**, 377–379.
29 S. M. Lee, B. S. Lee, T. G. Byun and K. C. Song, *Colloids Surf., A*, 2010, **355**, 167–171.
30 Y. Akamatsu, K. Makita, H. Inaba, H. Nakazumi and T. Minami, *J. Sol–Gel Sci. Technol.*, 2000, **19**, 387–391.
31 S. Hofacker and G. Schottner, *J. Sol-Gel Sci. Technol.*, 1998, **13**, 479–484.
32 G. Schottner, J. Kron and K. J. Deichmann, *Rev. Verre*, 2000, **6**, 38–41.
33 S. Lisinskia, J. Krauseb, D. Schanielb, L. Ratkea and T. Woikeb, *Scr. Mater.*, 2008, **58**, 553–555.
34 A. Fontana, E. Moser, F. Rossi, R. Campostrini and G. Carturan, *J. Non-Cryst. Solids*, 1997, **212**, 292–298.
35 S. O'Brien, M. Copuroglu and G. M. Crean, *Thin Solid Films*, 2007, **515**, 5439–544.
36 S. Jeong and J. Moon, *J. Non-Cryst. Solids*, 2005, **351**, 3530–3535.

37 J.-S. Kim, S.-C. Yang and B.-S. Bae, *Chem. Mater.*, 2010, **22**, 3549–3555.

38 J.-S. Kim, S.-C. Yang and B.-S. Bae, *J. Sol-Gel Sci. Technol.*, 2009, **53**, 434–440.

39 B. Meena, M. Takahashi, Y. Tokuda and T. Yoko, *Solid State Sci.*, 2008, **10**, 1200–1208.

40 S. O'Brien, M. Copuroglu and G. M. Crean, *Appl. Surf. Sci.*, 2007, **253**, 7969–7972.

41 W. Du, H. Wang, W. Zhong, L. Shen and Q. Du, *J. Sol-Gel Sci. Technol.*, 2005, **34**, 227–231.

42 F. Wanf, Z. Luo, S. Oing, Q. Qiu and R. Li, *J. Alloys Compd.*, 2009, **486**, 521–526.

43 X. Le Gueyel, S. Schutzmann, L. Stella, F. De Matteis, P. Proposito and M. Casalboni, *Opt. Mater.*, 2008, **31**, 451–454.

44 Y. Liu, C. Lue, M. Li, L. Zhang and B. Yang, *Colloids Surf., A*, 2008, **328**, 67–72.

45 Y. Han, J. Wakita, S. Kuroki, X. Wang and S. Ando, *J. Photopolym. Sci. Technol.*, 2008, **21**, 143–150.

46 D. J. Kang, T.-H. Lee and B.-S. Bae, *J. Sol-Gel Sci. Technol.*, 2004, **31**, 113–116.

47 K. Biswas, S. Ganpopadhyay, H.-C. Kim and R. D. Miller, *Thin Solid Films*, 2006, **514**, 350–354.

48 X. Zhang, C. Cao, B. Xiao, L. Yan, Q. Zhang and B. Jiang, *J. Sol-Gel Sci. Technol.*, 2009, **53**, 79–84.

49 C.-C. Chen, D.-J. Lin, T.-M. Don, F.-H. Huang and L.-P. Cheng, *J. Non-Cryst. Solids*, 2008, **354**, 3828–3835.

50 M. Faustini, L. Nicole, C. Boissière, P. Innocenzi, C. Sanchez and D. Grosso, *Chem. Mater.*, 2010, **22**, 4406–4413.

51 R. Himmelhuber, C. C. DeRose, R. A. Norwood and N. Peyghambanan, *Proc. SPIE–Int. Soc. Opt. Eng.*, 2008, **7049**, 70490G–70490G/10.

52 G. Schottner, J. Kron and K. Deichmann, *J. Sol-Gel Sci. Technol.*, 1998, **13**, 183–187.

53 G. Schottner, *Chem. Mater.*, 2001, **13**, 3422–3435.

54 J. L. Almaral-Sanchez, E. Rubio, A. Mendoza-Galvan and R. Ramirez-Bon, *J. Phys. Chem. Solids*, 2005, **66**, 1660–1667.

55 K. Wojtach, M. Laczka, K. Cholewa-Kowalska and J. Sokolowska, *J. Non-Cryst. Solids*, 2007, **353**, 2099–2103.

56 Y. Ivanova, H. Hristov, S. Handjieva and C. Petkov, *J. Optoelectron. Adv. Mater.*, 2005, **7**, 241–244.

57 M. Irie, *Chem. Rev.*, 2000, **100**, 1683–1716.

58 H. Durr and H. Bouas-Laurent, in *Photochromism: Molecules and Systems*, Revised edition, Elsevier Science, Amsterdam, 2003, ISBN 978-0444513229.

59 R. A. Evans, T. L. Hanley, M. A. Skidmore, T. P. Davis, G. K. Such, L. H. Yee, G. E. Ball and D. A. Lewis, *Nat. Mater.*, 2005, **4**, 249–253.

60 G. K. Such, R. A. Evans and T. P. Davis, *Macromolecules*, 2006, **39**, 1391–1396.

61 D. Levy, *Chem. Mater.*, 1997, **9**, 2666–2670.

62 L. Hou, M. Mennig and H. Schmidt, *Chim. Chron.*, 1994, **23**, 175–180.

63 R. Nakao, N. Ueda, Y. Abe, T. Horii and H. Inoue, *Polym. Adv. Technol.*, 1994, **5**, 240–241.

64 B. Schaudel, C. Guermeur, C. Sanchez, K. Nakatani and J. A. Delaire, *J. Mater. Chem.*, 1997, **7**, 61–65.

65 J. Biteau, F. Chaput, Y. Yokoyama and J. P. Boilot, *Chem. Lett.*, 1998, 359–360.

66 J. Biteau, F. Chaput and J. P. Boilot, *J. Phys. Chem.*, 1996, **100**, 9024–9031.

67 R. Nakao, N. Ueda, Y. S. Abe, T. Horii and H. Inoue, *Polym. Adv. Technol.*, 1996, **7**, 863–866.

68 L. Hou and H. Schmidt, *J. Mater. Sci.*, 1996, **31**, 3427–3434.

69 A. Zelichenok, F. Buchholtz, S. Yitzchaik, J. Ratner, M. Safro and V. Krongauz, *Macromolecules*, 1992, **25**, 3179–3183.

70 A. Klukowska, U. Posset, G. Schottner, M. L. Wis, C. Salemi-Delvaux and V. Malatesta, *Mater. Sci.*, 2002, **20**, 95–104.

71 M. Mennig, K. Fries, M. Lindenstruth and H. Schmidt, *Thin Solid Films*, 1999, **351**, 230–234.

72 L. Hou and H. Schmidt, *J. Mater. Sci. Lett.*, 1997, **16**, 435–436.

73 L. Hou, H. Schmidt, B. Hoffmann and M. Mennig, *J. Sol–Gel Sci. Technol.*, 1997, **8**, 927–929.

74 R. Pardo and D. Levy, *J. Mater. Chem.*, 2009, **19**, 6756–6760.

75 R. Pardo, M. Zayat and D. Levy, *C. R. Chim.*, 2010, **13**, 212–226.

76 R. Pardo, M. Zayat and D. Levy, *J. Sol-Gel Sci. Technol.*, 2006, **40**, 365–370.

77 A. Alvarez-Herrero, D. Garranzo, R. Pardo, M. Zayat and D. Levy, *Phys. Status Solidi C*, 2008, **5**, 1160–1163.

78 R. Pardo, M. Zayat and D. Levy, *J. Mater. Chem.*, 2006, **16**, 1734–1740.

79 R. Pardo, M. Zayat and D. Levy, *J. Mater. Chem.*, 2005, **15**, 703–708.

80 M. Zayat, R. Pardo and D. Levy, *J. Mater. Chem.*, 2003, **13**, 2899–2903.

81 T. Cheng, T. Lin, R. Brady and X. Wang, *Fibers Polym.*, 2008, **9**, 301–306.

82 T. Cheng, T. Lin, R. Brady and X. Wang, *Fibers Polym.*, 2008, **9**, 521–526.

83 N. Anderson, P. C. A. Alberius, J. Skov Pedersen and L. Bergstroem, *Microporous Mesoporous Mater.*, 2004, **72**, 175–183.

84 L. Raboin, M. Matheron, J. Biteau, T. Gacoin and J.-P. Boilot, *J. Mater. Chem.*, 2008, **18**, 3242–3248.

85 G. Winsberger, B. J. Scott, B. F. Chmelka and G. D. Stucky, *Adv. Mater.*, 2000, **12**, 1450–1454.

86 J. Biteau, F. Chaput, Y. Yokoyama and J.-P. Boilot, *Chem. Lett.*, 1998, 359–360.

87 J. Biteau, F. Chaput, K. Lahlil, J.-P. Boilot, G. M. Tsivgoulis, J.-M. Lehn, B. Darraq, C. Marois and Y. Lévy, *Chem. Mater.*, 1998, **10**, 1945–351.

88 C. Sanchez, A. Lafuma, L. Rozes, K. Nakatani, J. A. Delaire, E. Condoncillo, B. Viana and P. Escribano, in *Organic-Inorganic Hybrids for Photonics*, ed. L. Hubert and S. I. Najafi, SPIE, Washington, DC, 1998, vol. 3469, p. 192.

89 F. Chaput, J. Biteau, K. Lahlil, J. P. Boilot, B. Darracq, Y. Levy, J. Perelti, V. I. Safarov, G. Parent and A. Fernandez-Acebes, *Mol. Cryst. Liq. Cryst.*, 2000, **344**, 77–82.

90 B. Darraq, F. Chaput, K. Lahlil, Y. Levy and J. P. Boilot, *Adv. Mater.*, 1998, **10**, 1133–1136.

91 N. Landraud, J. Peretti, F. Chaput, G. Lamoel, J.-P. Boilot, K. Lahlil and V.I. Safarov, *Appl. Phys. Lett.*, 2001, **79**, 4562–4564.

92 F. Fabbri, Y. Lassailly, K. Lahlil, J. P. Boilot and J. Peretti, *Appl. Phys. Lett.*, 2010, **96**, 081908–081908/3.

93 M. Serwadczak and S. Kucharski, *J. Sol-Gel Sci. Technol.*, 2006, **37**, 57–62.

94 (*a*) M. Sun, W. Que and X. Hu, *J. Sol-Gel Sci. Technol.*, 2009, **50**, 415–420; (*b*) H. R. S. Mahdavi, E. Mohajerani, M. Mohseni and Y. Aghili, *J. Sol-Gel Sci. Technol.*, 2009, **52**, 82–87; (*c*) B. Comary, I. Malfant and L. Valade, *J. Sol-Gel Sci. Technol.*, 2009, **52**, 19–23.

95 S. Katayama, N. Yamada, K. Kikuta and M. Awano, *J. Ceram. Soc. Jpn.*, 2006, **114**, 114–119.

96 Y. Huang, Q. Y. Pan, X. W. Dong and X. Zhi, *Mater. Chem. Phys.*, 2006, **97**, 431–436.

97 W. Qi, H. Li and L. Wu, *J. Phys. Chem. B*, 2008, **112**, 8257–8263.

98 Z. Luo, J. Yang, H. cal, H. Li, X. Ren, J. Liu and X. Liang, *Thin Solid Films*, 2008, **516**, 5541–5544.

99 D. Avnir, *Acc. Chem. Res.*, 1995, **28**, 328–334.

100 Kobayashi, Y. Kurokawa, Y. Imai and S. Muto, *J. Non-Cryst. Solids*, 1988, **105**, 198–200.

101 R. Reisfeld, D. Brusilovsky, M. Eyal, E. Miron, Z. Burstein and J. Ivri, *Chem. Phys. Lett.*, 1989, **160**, 43–44.

102 F. Salin, G. Le Saux, P. Georges, A. Brun, C. Bagnall and J. Zarzycki, *Opt. Lett.*, 1989, **14**, 785–787.

103 E. T. Knobb, B. Dunn, F. Fuqua, F. Nishida and J. I. Zink, in *Ultrastructural Processing of Advanced Materials*, ed. D. R. Uhlmann and D. R. Uhlrich, Wiley-VCH Publisher, New York, 1992, p. 519.

104 B. Dunn and J. I. Zink, *J. Mater. Chem.*, 1991, **1**, 903–913.

105 J. I. Zink and B. Dunn, in *Sol–Gel Optics, Processing and Applications*, ed. L. Klein, Kluwer Academic Publishers, Dordrecht, 1994, p. 303.

106 T. Suratwala, Z. Gardlund, K. Davidson, D. R. Uhlmann, S. Bonilla and N. Peyghambarian, *J. Sol–Gel Sci. Technol.*, 1997, **8**, 973–978.

107 M. Faloss, M. Canva, P. Georges, A. Brun, F. Chaput and J.-P. Boilot, *Appl. Opt.*, 1997, **36**, 6760–6763.

108 R. Reisfeld and G. Seybold, *Chimia*, 1990, **44**, 295–298.

109 R. E. Hermes, T. H. Allik, S. Chandra and J. A. Hutchinson, *Appl. Phys. Lett.*, 1993, **63**, 877–879.
110 M. D. Rhan, T. A. King, C. A. Capozzi and A. B. Seddon, in *Sol–Gel Optics III*, ed. J. D. Mackenzie, SPIE, Washington, DC, 1994, vol. 2288, p. 364.
111 M. Canva, P. Georges, J.-F. Perelgritz, A. Brun, F. Chaput and J.-P. Boilot, *Appl. Opt.*, 1995, **34**, 428–431.
112 R. Reisfeld, D. Brusilovsky, M. Eyal, E. Miron, Z. Burstein and J. Irvi, *Chem. Phys. Lett.*, 1989, **160**, 43–44.
113 D. Shamrakov and D. Reisfeld, *Chem. Phys. Lett.*, 1993, **213**, 47–54.
114 J. Irvi, Z. Burstein, E. Miron, R. Reisfeld and M. Eyal, *IEEE J. Quantum Electron.*, 1990, **26**, 1516.
115 M. D. Rhan, T. A. King, A. A. Gorman and I. Hamblett, *Appl. Opt.*, 1997, **36**, 5862–5871.
116 S. Schultheiss, E. Yariv, R. Reisfeld and H. Dieterbeuer, *Photochem. Photobiol. Sci.*, 2002, **1**, 320–323.
117 B. Lebeau, N. Herlet, J. Livage and C. Sanchez, *Chem. Phys. Lett.*, 1993, **206**, 15–20.
118 B. Dunn, F. Nishida, A. Toda, J. I. Zink, T. Allik, S. Chandra and J. Hutchinson, *Mater. Res. Soc. Symp. Proc.*, 1994, **329**, 267.
119 F. Del Monte and D. Levy, *Chem. Mater.*, 1995, **7**, 292.
120 M. Casalboni, F. De Matteis and P. Proposito, *Appl. Phys. Lett.*, 1999, **75**, 2172.
121 R. Reisfeld, A. Weiss, T. S. Idarov, E. Yariv and A. A. Ishchenko, *Polym. Adv. Technol.*, 2004, **15**, 291–301.
122 A. M. Weiss, T. Saraidarov and R. Reisfeld, *Opt. Mater.*, 2001, **16**, 15–20.
123 G. Garcia, R. Sastre, A. Costella and I. Garcia-Moreno, *Adv. Funct. Mater.*, 2008, **18**, 2017–2025.
124 T. H. Nhung, *Commun. Phys.*, 2005, **15**, 75–84.
125 T. H. Nhung, *Commun. Phys.*, 2005, **15**, 39–47.
126 T. H. Nhung, M. Canva, F. Chaput, H. Goudet, G. Roger, A. Brun, D. D. Manh, D. Nguyen and J.-P. Boilot, *Opt. Commun.*, 2004, **232**, 343–351.
127 C. M. Carbonaro, A. Anedda, S. Gandi and A. Magistris, *J. Phys. Chem. B*, 2006, **110**, 12932–12937.
128 T. H. Nhung, M. Canva, T. T. A. Truong, F. Chaput, A. Brun, N. D. Hung and J.-P. Boilot, *Appl. Opt.*, 2003, **42**, 2213–2218.
129 M. Berard, V. Rachel, K. Lahlil, T. Gacoin, J. Galaup and J.-P. Boilot, *Proc. SPIE–Int. Soc. Opt. Eng.*, 2007, **6638**, 66380S–66380S/9.
130 S. Garcia-Revilla, J. Fernandez, M. A. Lliarramendi, B. Garcia-Ramiro, R. Slada, H. Cui, M. Zayat and D. Levy, *Opt. Express*, 2008, **16**, 12251–12263.
131 A. E. Siegmann, *Lasers*, University Science Books, Mill Valley, CA, 1986.
132 P. D. Yang, G. Wirnsberger, H. C. Huang, S. R. Cordero, M. D. McGehee, B. Scott, T. Deng, G. M. Whitesides, B. F. Chmelka, S. K. Buratto and G. D. Stucky, *Science*, 2000, **287**, 465–467.
133 A. Donval, D. Josse, G. Kranzelbinder, R. Hierle, E. Toussaere, J. Zyss, G. Perpelitsa, O. Levi, D. Davidov, I. Bar-Nahum and R. Neumann, *Synth. Met.*, 2001, **124**, 59–61.
134 H. A. S. Al-shamiri, I. M. Azzouz, M. S. Shafik and Y. A. Badr, *J. Sol-Gel Sci. Technol.*, 2006, **41**, 65–69.
135 Y. Yang, C. Ye, W. Ni, K. Y. Wong, M. Wang, D. Lo and G. Qian, *J. Sol-Gel Sci. Technol.*, 2007, **44**, 53–57.
136 M. H. Bartl, S. W. Boettcher, E. L. Hu and G. D. Stucky, *J. Am. Chem. Soc.*, 2004, **126**, 10826–10827.
137 T. Kazes, T. Saraidarov, R. Reisfeld and U. Banim, *Adv. Mater.*, 2009, **21**, 1716–1720.
138 T. Saraidarov and R. Reisfeld, *Opt. Lett.*, 2006, **31**, 356–358.
139 M. Hayden, *Nat. Photonics*, 2007, **1**, 138–139.
140 R. Buestrich, F. Kahlenberg, M. Popall, P. Dannberg, R. Müller-Fiedler and O. Rösch, *J. Sol-Gel Sci. Technol.*, 2001, **20**, 181–186.
141 H. Ma, A. K.-Y. Jen and L. R. Dalton, *Adv. Mater.*, 2002, **14**, 1339–1365.
142 M. Popall, R. Houbertz, L. Fröhlich, U. Streppel, P. Dannberg, S. Westenhofer and M. Gale, *Glass Sci. Technol.*, 2003, **76**, 53–58.
143 K. Richardson, D. Krol and K. Hirao, *Int. J. Appl. Glass Sci.*, 2010, **1**, 74–86.
144 K. Lee, D. Lim, L. Kimerling, J. Shin and F. Cerrina, *Opt. Lett.*, 2001, **26**, 1888–1890.
145 P. Innocenzi, A. Martucci, M. Guglielmi, L. Armelao, S. Pelli, G. C. Righini and G. C. Battaglin, *J. Non-Cryst. Solids*, 1999, **259**, 182–190.
146 S. Costacurta, L. Malfatti, P. Falcaro and P. Innocenzi, *J. Sol-Gel Sci. Technol.*, 2007, **44**, 59–64.
147 P. Innocenzi, M. Esposto and A. Maddalena, *J. Sol-Gel Sci. Technol.*, 2001, **20**, 293–301.
148 P. Innocenzi, T. Kidchob and T. Yoko, *J. Sol-Gel Sci. Technol.*, 2005, **35**, 225–235.
149 (*a*) B. Alonso, D. Massiot, M. Valentini, T. Kidchob and P. Innocenzi, *J. Non-Cryst. Solids*, 2008, **354**, 1615–1626; (*b*) M. Templin, U. Wiesner and H. W. Spiess, *Adv. Mater.*, 1997, **9**, 814–816; (*c*) B. Riegel, S. Blittersdorf, W. Kiefer, S. Hofacker, M. Muller and G. Schottner, *J. Non-Cryst. Solids*, 1998, **226**, 76–80; (*d*) P. Innocenzi, G. Brusatin, M. Guglielmi and R. Bertani, *Chem. Mater.*, 1999, **11**, 1672–1679; (*e*) P. Innocenzi, A. Sassi, G. Brusatin, M. Guglielmi, D. Favretto, R. Bertani, A. Venzo and F. Babonneau, *Chem. Mater.*, 2001, **13**, 3635–3643.
150 R. Copperwhite, M. Oubaha, D. L. Versace, C. Croutxe-Barghorn and B. D. MacCraith, *J. Non-Cryst. Solids*, 2008, **354**, 3617–3622.
151 X. Le Guevel, C. Palazzesi, P. Prosposito, G. Della Giustina and G. Brusatin, *J. Mater. Chem.*, 2008, **18**, 3556–3562.
152 P. Innocenzi, G. Brusatin and F. Babonneau, *Chem. Mater.*, 2000, **12**, 3726–3732.
153 R. Houbertz, G. Domann, C. Cronauer, A. Schmitt, H. Martin, J.-U. Park, L. Fröhlich, R. Buestrich, M. Popall, U. Streppel, P. Dannberg, C. Wachter and A. Brauer, *Thin Solid Films*, 2003, **442**, 194–200.
154 X. Zhang, H. Lu, A. M. Soutar and X. Zeng, *J. Mater. Chem.*, 2004, **14**, 357–361.
155 J. Kyung Ho and B.-S. Bae, *J. Appl. Polym. Sci.*, 2008, **108**, 3169–3176.
156 S. Y. Kim, S. Augustine, Y. J. Kim, B. S. Bae, S. I. Woo and J. K. Kang, *J. Phys. Chem. B*, 2005, **109**, 9397–9401.
157 E. Wipfelder and K. Hohn, *Angew. Makromol. Chem.*, 1994, **218**, 111–115.
158 E.-S. Kang, M. Takahashi, Y. Tokuda and Toshinobu Yoko, *J. Mater. Res.*, 2006, **21**, 1286–1293.
159 J. Jabbour, S. Calas, S. Gatti, R. K. Kribich, M. Myara, G. Pille, P. Etienne and Y. Moreau, *J. Non-Cryst. Solids*, 2008, **354**, 651–658.
160 X. Zhang, Z. Zhao, M. Qian, R. Yin, X. Zeng and P. Plante, *IEEE Conferences Proceedings: Microwave Photonics, 2006. MWP'06. International Topical Meeting*, 2006, pp. 1–4.
161 J.-I. Jung, O.-H. Park and B.-S. Bae, *J. Sol-Gel Sci. Technol.*, 2003, **26**, 897–901.
162 Y. K. Kwon, J. K. Han, J. M. Lee, Y. S. Ko, J. H. Oh, H.-S. Lee and E.-H. Lee, *J. Mater. Chem.*, 2008, **18**, 579–585.
163 O. Soppera, C. Croutxé-Barghorn, C. Carré and D. Blanc, *Appl. Surf. Sci.*, 2002, **186**, 91.
164 M. Feuillade, C. Croutxé-Barghorn, L. Mager, C. Carré and A. Fort, *Chem. Phys. Lett.*, 2004, **398**, 151–156.
165 D. Buso, G. Della Giustina, G. Brusatin, M. Guglielmi, A. Martucci, A. Chiasera, Alessandro, M. Ferrari and F. Romanato, *J. Nanosci. Nanotechnol.*, 2009, **9**, 1858–1864.
166 G. Della Giustina, G. Brusatin, M. Guglielmi and F. Romanato, *Mater. Sci. Eng., C*, 2007, **27**, 1382–1385.
167 G. Della Giustina, M. Prasciolu, G. Brusatin, M. Guglielmi and F. Romanato, *Microelectron. Eng.*, 2009, **86**, 745–748.
168 S. K. Pani, Y. Quiling, C. C. Wong, D. K. Y. Low, X. Zhang and M. K. Iyer, *Thin Solid Films*, 2006, **504**, 336–340.
169 P. Falcaro and P. Innocenzi, *J. Sol–Gel Sci. Technol.*, 2010, DOI: 10.1007/s10971-009-2127-7.
170 S. Costacurta, L. Malfatti, A. Patelli, P. Falcaro, H. Amenitsch, B. Marmiroli, G. Grenci, M. Piccinini and P. Innocenzi, *Plasma Processes Polym.*, 2010, **7**, 459–465.
171 P. Falcaro, L. Malfatti, H. Amenitsch, B. Marmioli, G. Grenci and P. Innocenzi, *Adv. Mater.*, 2009, **21**, 4932–4936.
172 S. Costacurta, L. Malfatti, P. Falcaro and P. Innocenzi, *J. Sol-Gel Sci. Technol.*, 2007, **44**, 59–64.
173 O.-H. Park, S.-J. Kim and B.-S. Bae, *J. Mater. Chem.*, 2004, **14**, 1749–1753.

174 M. Takahashi, T. Maeda, K. Uemura, J. Yao, Y. Tokuda, T. Yoko, H. Kaji, A. Marcelli and P. Innocenzi, *Adv. Mater.*, 2007, **19**, 4343–4346.
175 J. Lim, M. Popall and S. Kang, *IEEE Trans. Magn.*, 2009, **45**, 2300–2303.
176 L. Prod'homme, *Phys. Chem. Glasses*, 2004, **4**, 357–362.
177 (*a*) E.-S. Kang, J. Y. Bae and B.-S. Bae, *J. Sol-Gel Sci. Technol.*, 2003, **26**, 981–984; (*b*) E.-S. Kang, T.-H. Lee and B.-S. Bae, *Appl. Phys. Lett.*, 2002, **81**, 1438–1440.
178 Wang, X. Xu, L. Li, D. Liu and L. W. Wencheng, *J. Appl. Phys.*, 2003, **94**, 4228–4230.
179 L. B. Soldano and E. C. M. Pennings, *J. Lightwave Technol.*, 1995, **13**, 615–627.
180 Y. Wang, Y. D. Wu, J.-G. Li, H.-J. Wang and X.-W. Hu, *Chin. Phys. Lett.*, 2008, **25**, 3693–3695.
181 Y. Zhang, X. Wu, Z. He, L. Liu and X. Lei, *J. Opt. A: Pure Appl. Opt.*, 2009, **11**, 105401.
182 J. H. Kim, B. W. Dudley and P. J. Moyer, *J. Lightwave Technol.*, 2006, **24**, 612–616.
183 X. Zhang, Z. Zhao, M. Qian, S. Y. Lee, M. K. Chin, X. Zeng, D. K. Y. Low, A. C. W. Lu and P. Plante, *J. Cryst. Growth*, 2006, **288**, 176–179.
184 M. A. Fardad, O. V. Mishechkin and M. Fallahi, *J. Lightwave Technol.*, 2001, **19**, 84–91.
185 O. V. Mishechkin and M. Fallahi, *Opt. Eng.*, 2004, **43**, 662–666.
186 J. Porque, P. Coudray, R. Charters, K. Kribich, P. Etienne and Y. Moreau, *Opt. Commun.*, 2000, **183**, 45–49.
187 B. Boury, R. J. P. Corriu, V. Le Strat, P. Delord and M. Nobili, *Angew. Chem., Int. Ed.*, 1999, **38**, 3172.
188 J. J. E. Moreau, B. P. Pichon, M. Wong Chi Man, C. Bied, H. Prizkow, J.-L. Bantignies, P. Dieudonne and J.-L. Sauvajol, *Angew. Chem., Int. Ed.*, 2004, **43**, 203.
189 K. Okamoto, M. P. Kapoor and S. Inagaki, *Chem. Commun.*, 2005, 1423.
190 J. J. E. Moreau, B. P. Pichon, G. Arrachart, M. Wong Chi Man and C. Bied, *New J. Chem.*, 2005, **29**, 653.
191 F. Lerouge, G. Cerveau and R. J. P. Corriu, *New J. Chem.*, 2006, **30**, 1364–1376.
192 J. J. E. Moreau, L. Vellutini, M. Wong Chi Man and C. Bied, *J. Am. Chem. Soc.*, 2001, **123**, 1509.
193 M. Ogawa and K. Kuroda, *Chem. Rev.*, 1995, **95**, 399.
194 S. Inagaki, Shiyou Guan, T. Ohsuna and O. Terasaki, *Nature*, 2002, **416**, 304–307.
195 B. Menaa, M. Takahashi, P. Innocenzi and T. Yoko, *Chem. Mater.*, 2007, **19**, 1946.
196 (*a*) C. Figus, M. Takahashi, T. Kidchob, T. Yoko, M. Piccinini, M. F. Casula and P. Innocenzi, *J. Sol-Gel Sci. Technol.*, 2009, **52**, 408; (*b*) P. Innocenzi, C. Figus, T. Kidchob, M. Valentini, B. Alonso and M. Takahashi, *Dalton Trans.*, 2009, 9146.
197 M. Takahashi, C. Figus, T. Kidchob, S. Enzo, M. Casula, M. Valentini and P. Innocenzi, *Adv. Mater.*, 2009, **21**, 1732–5.
198 C. McDonagh, C. S. Burke and B. D. MacCraith, *Chem. Rev.*, 2008, **108**, 400–422.
199 K. R. Kribich, R. Copperwhite, H. Barry, B. Kolodziejczyk, J.-M. Sabattié, K. O'Dwyer and B. D. MacCraith, *Sens. Actuators, B*, 2005, **107**, 188–192.
200 F. Pang, X. Han, F. Chu, J. Geng, H. Cai, R. Qu and Z. Fang, *Sens. Actuators, B*, 2007, **120**, 610–614.
201 P. J. Skrdla, S. B. Mendes, N. R. Armstrong and S. S. Saavedra, *J. Sol-Gel Sci. Technol.*, 2002, **24**, 167–173.
202 P. L. Edmiston, D. P. Campbell, D. S. Gottfried, J. Baughman and M. M. Timmers, *Sens. Actuators, B*, 2010, **143**, 574–582.
203 D. Blanc, S. Pelissier, K. Saravanamuttu, S. I. Najafi and M. P. Andrews, *Adv. Mater.*, 1999, **11**, 1508–1511.
204 D. J. Kang and B.-S. Bae, *Acc. Chem. Res.*, 2007, **40**, 903.
205 K. Shinmou, K. Nakama and T. Koyama, *J. Sol-Gel Sci. Technol.*, 2000, **19**, 267–272.
206 N. Tohge, R. Ueno, F. Chiba, K. Kintaka and J. Nishii, *J. Sol-Gel Sci. Technol.*, 2000, **19**, 119–123.
207 Y. Haruvy, I. Gilath, M. Maniewictz and N. Eisenberg, *Chem. Mater.*, 1997, **9**, 2604–2615.
208 H. Jiang, X. Yuan, Z. Yun, Y.-C. Chan and Y. L. Lam, *Mater. Sci. Eng., C*, 2001, **16**, 99–102.
209 A. H. O. Kärkkäinen, J. T. Rantala, A. Maaninen, G. E. Jabbour and M. R. Descour, *Adv. Mater.*, 2002, **14**, 535–540.
210 A. H. O. Kärkkäinen, J. T. Rantala, J. M. Tamkin and M. R. Descour, *J. Lightwave Technol.*, 2003, **21**, 614–623.
211 S. Dal Zilio, G. Della Giustina, G. Brusatin and M. Tormen, *Microelectron. Eng.*, 2010, **87**, 1143–1146.
212 B.-S. Bae, *J. Sol-Gel Sci. Technol.*, 2004, **31**, 309–315.
213 W. Yu and X.-C. Yuan, *J. Mater. Chem.*, 2004, **14**, 821–823.
214 S. Maruo, O. Nakamura and S. Kawata, *Opt. Lett.*, 1997, **22**, 132–134.
215 M. Farsari and B. N. Chichkov, *Nat. Photonics*, 2009, **3**, 450–452.
216 R. Houbertz, L. Fröhlich, M. Popall, U. Steppel, P. Dannberg, A. Bräuer, J. Serbin and B. N. Chichkov, *Adv. Eng. Mater.*, 2003, **5**, 551–555.
217 B. Bhuian, R. J. Winfield, S. O. Brien and G. M. Crean, *Appl. Surf. Sci.*, 2006, **252**, 4845–4849.
218 A. Ovsianikov, X. Shizhou, M. Farsari, M. Vamvakaki, C. Fotakis and Boris N. Chichkov, *Opt. Express*, 2009, **17**, 2143–2148.
219 H. Segawa, K. Yoshida, T. Kondo, S. Matsuo and H. Misawa, *J. Sol-Gel Sci. Technol.*, 2003, **26**, 1023–1027.
220 M. Malinauskas, H. Gilbergs, A. Zukauskas, V. Purlys, D. Paipulas and R. Gadonas, *J. Opt.*, 2010, **12**, 035204-12.
221 S. Krivec, N. Matsko, V. Satzinger, N. Pucher, N. Galler, T. Koch, V. Schmidt, W. Grogger, R. Liska and H. C. Lichtenegger, *Adv. Funct. Mater.*, 2010, **20**, 811–819.
222 R. Infhur, J. Stampfl, S. Krivec, R. Liska, H. Lichtenegger, V. Satzinger, V. Schmidt, N. Matsko and W. Grogger, *Mater. Res. Soc. Symp. Proc.*, 2009, **1179**, BB01–07.
223 A. Ovsianikov, J. Viertl, B. Chichkov, M. Oubaha, B. MacCraith, I. Sakellari, A. Giakoumaki, D. Gray, M. Vamvakaki, M. Farsari and C. Totakis, *ACS Nano*, 2008, **2**, 2257–2262.
224 S. D. Gittard, A. Ovsianikov, B. N. Chichkov, A. Doraiswamy and R. J. Narayan, *Expert Opin. Drug Delivery*, 2010, **7**, 513–533.
225 M. Farsari, A. Ovsianikov, M. Vamvakaki, I. Sakellari, D. Gray, B. N. Chichkov and C. Fotakis, *Appl. Phys. A: Mater. Sci. Process.*, 2008, **93**, 11–15.
226 J. Clark and G. Lanzani, *Nat. Photonics*, 2010, **4**, 438–446.
227 F. Chaumel, H. Jiang and A. Kakkar, *Chem. Mater.*, 2001, **13**, 3389–3395.
228 L. R. Dalton, P. A. Sullivan and D. H. Bale, *Chem. Rev.*, 2010, **110**, 25–55.
229 A. W. Harper, S. Sun, L. R. Dalton, S. M. Garner, A. Chen, S. Kalluri, W. H. Steier and B. H. Robinson, *J. Opt. Soc. Am. B*, 1998, **15**, 329–337.
230 The order parameter is defined as $\phi = (1 - A_1)/A_0$, where A_0 and A_1 are the absorbances before and after poling.
231 K.-S. Lee, T.-D. Kim, Y. H. Min and C. S. Yoon, *Synth. Met.*, 2001, **117**, 311–313.
232 H. K. Kim, S.-J. Kang, S.-K. Choi, Y.-H. Min and C. S. Yoon, *Chem. Mater.*, 1999, **11**, 779–788.
233 W. Gao, J. Sun, X. Sun, Y. Yan, L. Gao and D. Zhang, *Microwave Opt. Technol. Lett.*, 2009, **51**, 2097–2100.
234 Y. Cui, G. Qian, L. Chen, Z. Wang and M. Wang, *Dyes Pigm.*, 2008, **77**, 217–222.
235 Y. Cui, G. Qian, L. Chen, J. Gao and M. Wang, *Opt. Commun.*, 2007, **270**, 414–418.
236 H. Zhang, D. Lu and M. Fallahi, *Opt. Mater.*, 2006, **28**, 992–999.
237 B. Lebeau, S. Brasselet, J. Zyss and C. Sanchez, *Chem. Mater.*, 1997, **9**, 1012–1020.
238 B. Lebeau, C. Sanchez, S. Brasselet, J. Zyss, G. Froc and M. Dumont, *New J. Chem.*, 1996, **20**, 13–19.
239 H. Jiang and A. K. Kakkar, *Adv. Mater.*, 1998, **10**, 1093–1097.
240 P.-H. Chang, H.-C. Tsai, Y.-R. Chen, J.-Y. Chen and G.-H. Hsiue, *Langmuir*, 2008, **24**, 11921–11927.
241 H. Zhang and M. Fallahi, *Opt. Commun.*, 2005, **248**, 415–418.
242 D. Imaizumi, T. Hayakawa, T. Kasuga and M. Nogami, *J. Sol-Gel Sci. Technol.*, 2000, **19**, 383–386.
243 D. Wang, X. Chen, X. Zhang, W. Wang, Y. Liu and L. Hua, *Curr. Appl. Phys.*, 2009, **9**, S170–S173.
244 Y. Cui, B. Li, C. Yu, J. Yu, J. Gao, M. Yan, G. Chen, Z. Wang and G. Qian, *Thin Solid Films*, 2009, **517**, 5075–5078.
245 J. Yu, Y. Cui, J. Gao, Z. Wang and G. Qian, *J. Phys. Chem. B*, 2009, **113**, 14877–14883.
246 X. Jin, Y. Cui, J. Gao, J. Nie, W. Liu and G. Qian, *Thin Solid Films*, 2009, **517**, 5079–5083.

247 L. Chen, G. Qian, X. Jin, Y. Cui, J. Gao, Z. Wang and M. Wang, *J. Phys. Chem. B*, 2007, **111**, 3115–3121.

248 Y.-C. Chen, Y.-J. Yang, T.-Y. Juang, L.-H. Chan, S. A. Dai, F. M. C. Chen, W.-C. Su and R.-J. Jeng, *Synth. Met.*, 2009, **159**, 1852–1858.

249 Chromophores that have a donor (push) and an acceptor group (pull) at the extremities of the molecule are indicated as push–pull.

250 (*a*) A. Abbotto, S. Bradamante, A. Facchetti and G. A. Pagani, *J. Org. Chem.*, 1997, **62**, 5755–5765; (*b*) A. Abbotto, S. Bradamante, A. Facchetti, G. A. Pagani, I. Ledoux and J. Zyss, *Mater. Res. Soc. Symp. Proc.*, 1998, **488**, 819–822.

251 (*a*) P. Innocenzi, E. Miorin, G. Brusatin, A. Abbotto, L. Beverina, G. A. Pagani, M. Casalboni, F. Sarcinelli and M. Pizzoferrato, *Chem. Mater.*, 2002, **14**, 3758–3766; (*b*) P. Innocenzi, G. Brusatin, A. Abbotto, L. Beverina, G. A. Pagani, M. Casalboni, F. Sarcinelli and M. Pizzoferrato, *J. Sol-Gel Sci. Technol.*, 2003, **26**, 967–970.

252 (*a*) G. Brusatin, P. Innocenzi, L. Beverina, G. Pagani, A. Abbotto, F. Sarcinelli and M. Casalboni, *J. Non-Cryst. Solids*, 2004, **345–346**, 575–579; (*b*) G. Brusatin, A. Abbotto, L. Beverina, G. A. Pagani, M. Casalboni, F. Sarcinelli and P. Innocenzi, *Adv. Funct. Mater.*, 2004, **14**, 1160–579; (*c*) G. Brusatin, P. Innocenzi, A. Abbotto, L. Beverina, G. A. Pagani, M. Casalboni, F. Sarcinelli and R. Pizzoferrato, *J. Eur. Ceram. Soc.*, 2004, **24**, 1853–1856.

253 Y. Enami, C. T. Derose, D. Mathine, C. Loychik, C. Greenlee, R. A. Norwood, T. D. Kim, J. Luo, Y. Tian, A. K.-Y. Jen and N. Peyghambarian, *Nat. Photonics*, 2007, **1**, 180–185.

254 (*a*) Y. Enami, G. Meredith, N. Peyghambarian, M. Kawazu and A. K.-Y. Jen, *Appl. Phys. Lett.*, 2003, **82**, 490–492; (*b*) Y. Enami, M. Kawazu, A. K.-Y. Jen, G. Meredith and N. J. Peyghambarian, *J. Lightwave Technol.*, 2003, **21**, 2053–2060; (*c*) Y. Enami, G. Meredith, N. Peyghambarian and A. K.-Y. Jen, *Appl. Phys. Lett.*, 2003, **83**, 4692–4694; (*d*) C. T. DeRose, Y. Enami, C. Loychik, R. A. Norwood, D. Mathine, M. Fallahi, N. Peyghambarian, J. D. Luo, A. K.-Y. Jen, M. Kathaperumal and M. Yamamoto, *Appl. Phys. Lett.*, 2006, **89**, 131102–131103.