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Host Matrix Materials for Luminescent Solar Concentrators: Recent Achievements and Forthcoming Challenges

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Luminescent solar concentrators (LSCs) have attracted increasing attention in the past few years as appealing solar energy technology for the seamless integration of photovoltaic (PV) systems into the built environment. Traditionally, research in this field has focused on two main aspects: the optimization of the device assembly, in the quest for more efficient architectures to maximize collection, transport, and conversion of photons into usable electrical energy; the development of novel, highly emissive luminescent species, to ensure broad light collection and efficient photon emission. Only recently, the attention has also been directed toward the selection and development of suitable host matrix/waveguide materials with appropriate optical properties, sufficient chemical compatibility with the guest luminescent species, good processability for easy device fabrication and prolonged durability in outdoor operation. In addition to consolidated polymeric systems based on polyacrylates or polycarbonates, in recent years different examples of alternative host matrix systems have been proposed, characterized by peculiar chemical, physical and optical characteristics specifically designed to meet the stringent requirements of the LSC technology. This mini-review will focus on recent developments in the design of new host matrix materials for LSC applications. An overview of the most recent examples of novel LSC host matrices will be provided here, mainly focusing on new polymers, polymer-based organic-inorganic hybrids and multifunctional organic systems. Finally, opportunities and challenges in the field will be considered in view of the effective exploitation of the LSC technology in real application scenarios.

Keywords: luminescent solar concentrator (LSC), photovoltaic (PV), solar cells (SC), waveguide (WG), polymer, organic-inorganic hybrid, multifunctional devices

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INTRODUCTION

Luminescent solar concentrators (LSCs) have been regarded as a promising, accessible solar energy technology for reducing architectural barriers to the integration of photovoltaic (PV) systems into the built environment (Meinardi et al., 2017).

Originally proposed in the late 70's (Weber and Lambe, 1976; Goetzberger and Greube, 1977), LSC systems typically consist in bulk slabs or thin films/coatings of a transparent host matrix material embedding luminescent species that act as light-harvesting and spectral-conversion

centers of the incident light. Upon light absorption, photons are re-emitted *via* radiative decay by these luminophores and a fraction of the downshifted light is confined within the host matrix as a result of the difference in refractive indexes between the LSC material and the surrounding (air) medium. Total internal reflection (TIR) allows such trapped photons to be conveyed in waveguide mode toward the edges of the LSC device, where they become concentrated and can be collected by small-area optically-coupled solar cells for photon-to-electron conversion

In the past decade, research has pushed forward the performance of LSCs making them closer to practical deployability on the market.

In this mini-review, the focus will be on recent developments in the design of new host/waveguide materials for LSC applications. This discussion will include new polymers, polymer-based organic-inorganic hybrids and multifunctional systems. Opportunities and challenges in the field will also be considered in view of the effective exploitation of the LSC technology in real-life scenarios.

LSC OPERATION AND HOST MATERIAL REQUIREMENTS

In general terms, the performance of LSC systems can be quantified based on the so-called optical efficiency of the LSC η_{opt}, which is a measure of the optical power effectively delivered at the edges of the LSC (P_{out}^{opt}) with respect to the optical power incident on its top surface (P_{in}^{opt}):

$$\eta_{opt} = P_{out}^{opt}/P_{in}^{opt} \quad (1)$$

This parameter provides a direct estimation of the fundamental properties of a LSC (i.e., to collect and concentrate incident light) as it is directly influenced by all intrinsic loss mechanisms occurring to photons prior to being successfully collected at the edges of the waveguide (Debije and Verbunt, 2012; Moraitis et al., 2018). To tackle some of these loss mechanisms, research in the field of LSCs has been traditionally driven by the development of highly emissive luminescent species and by the engineering of more efficient device assemblies, as recently summarized in some excellent review articles (Debije and Verbunt, 2012; McKenna and Evans, 2017; Mazzaro and Vomiero, 2018; Pucci, 2018).

The choice of the host/waveguide material employed for the LSC assembly has also a direct effect on efficiency as it can greatly impact the processes of photon harvesting (reflection and scattering losses are matrix-dependent), absorption/emission (photoluminescence quantum yield (PLQY) of the luminophore can be affected by its solubility in the host matrix material), waveguiding/collection at the LSC perimeter (TIR and parasitic absorption by the host matrix are determined by its optical properties) (Kastelijn et al., 2009). Host materials for LSC applications should be designed so as to provide simultaneously a number of desirable features (Zettl et al., 2017), including: suitable refractive index; high transmittance in the visible and near-infrared range; high thermodynamic solubility for the embedded luminescent species; suitable thermal properties (namely, thermo-oxidative stability, and glass transition temperature T_g) compatible with the conditions used for materials processing and with the target application; long-term durability in outdoor contexts.

Glass was originally considered a reference material for LSCs due to its excellent optical properties as well as unbeatable chemical, photochemical, and environmental stability. However, the high processing temperatures needed for the production of conventional glass together with its high specific weight have shifted the attention toward polymeric systems. In this area, commodity polymers such as poly(methyl methacrylate) (PMMA) or polycarbonate (PC) have been traditionally employed as inexpensive host waveguide materials in bulk LSCs or as easily processable host carriers in thin-film LSCs. To overcome some of the limitations of these conventional systems and to provide additional functionalities to the resulting LSC system, in recent years a surge of new alternative matrix systems has been proposed with chemical, physical, and optical characteristics appropriately designed to meet the specific requirements of the LSC technology, as will be discussed in the next sections.

POLYMERIC MATRICES

PMMA is by far the most widely employed host polymer for LSCs because of its excellent transparency to visible light and its suitable refractive index ($n \approx 1.5$) (Li et al., 2019). Recently, its use as host matrix material in bulk LSCs was benchmarked against other commodity thermoplastics with similarly suitable thermal characteristics [polystyrene (PS), styrene-acrylonitrile (SAN) and different classes of PC] in terms of optical properties, compatibility with the target luminescent species (Lumogen F 305 Red by BASF, LF305 from here on) and resulting optical efficiency (Zettl et al., 2017). It was found that PMMA and PC (compact-disc grade) displayed the highest output irradiance level from the LSC edges, in both cases yielding η_{opt} values of 8.9% with dye doping concentration of 500 ppm. This result was correlated with the high internal transmittance of these matrices, which enables strong absorption of incoming photons by the embedded fluorescent dye.

However, PMMA usefulness is limited by the poor solubility that efficient luminophores feature in such a matrix (Al-Kaysi et al., 2006; Colby et al., 2010; Yoo et al., 2010), as well as by its limited photostability, especially toward high energy UV light (Kaczmarek et al., 2000; Griffini et al., 2013a). Improving the stability of PMMA as host polymeric matrix for LSCs has been a key focus for many research groups in the last few years. In an early study (Mansour et al., 2005), a copolymer made of methyl methacrylate and styrene [poly(STY-co-MMA)] doped with three different organic dyes was developed and its photodegradative response was benchmarked against PMMA. It was shown that all tested copolymer/dye systems displayed much enhanced stability compared with PMMA homopolymer,

irrespectively from the type of dye employed, due to more favorable dye/matrix interactions.

More recently, crosslinked systems based on partially fluorinated polymers were presented as potential alternative host matrix materials for the fabrication of durable polymer-based LSC devices (Griffini et al., 2013b). The new host matrix systems were obtained by thermally crosslinking a functional chloro-trifluoro-ethylenevinyl-ether (CTFE–VE) copolymer with different types of aliphatic polyisocyanates. The resulting LSCs in thin-film configuration (with LF305 as fluorophore) were shown to yield superior long-term operational stability compared to PMMA-based devices without compromising the efficiency. Further work by the same group demonstrated that different crosslinking agents (isocyanate *vs.* melamine) play a role in the evolution of chemical, physical, and morphological properties of the CTFE–VE-based LSC coatings during weathering (Griffini et al., 2014).

In the field of cross-linked systems, an unsaturated polyester (UP) resin (a mixture of UP and STY with methyl ethyl ketone peroxide as thermal initiator) was proposed as a possible alternative LSC host material to more conventional PMMA (Lim et al., 2012). To enhance the optical properties of the host matrix, a blend between UP and MMA was proposed, embedding coumarin 6 as luminescent species and resulting in satisfactory absorption and emission response.

A different, interesting approach for the development of novel polymeric host matrix systems was recently proposed based on the use of poly(p-xylylene) (or parylene) (Maggioni et al., 2013). By employing a suitably developed vacuum-based co-sublimation process, the parylene-based host material and

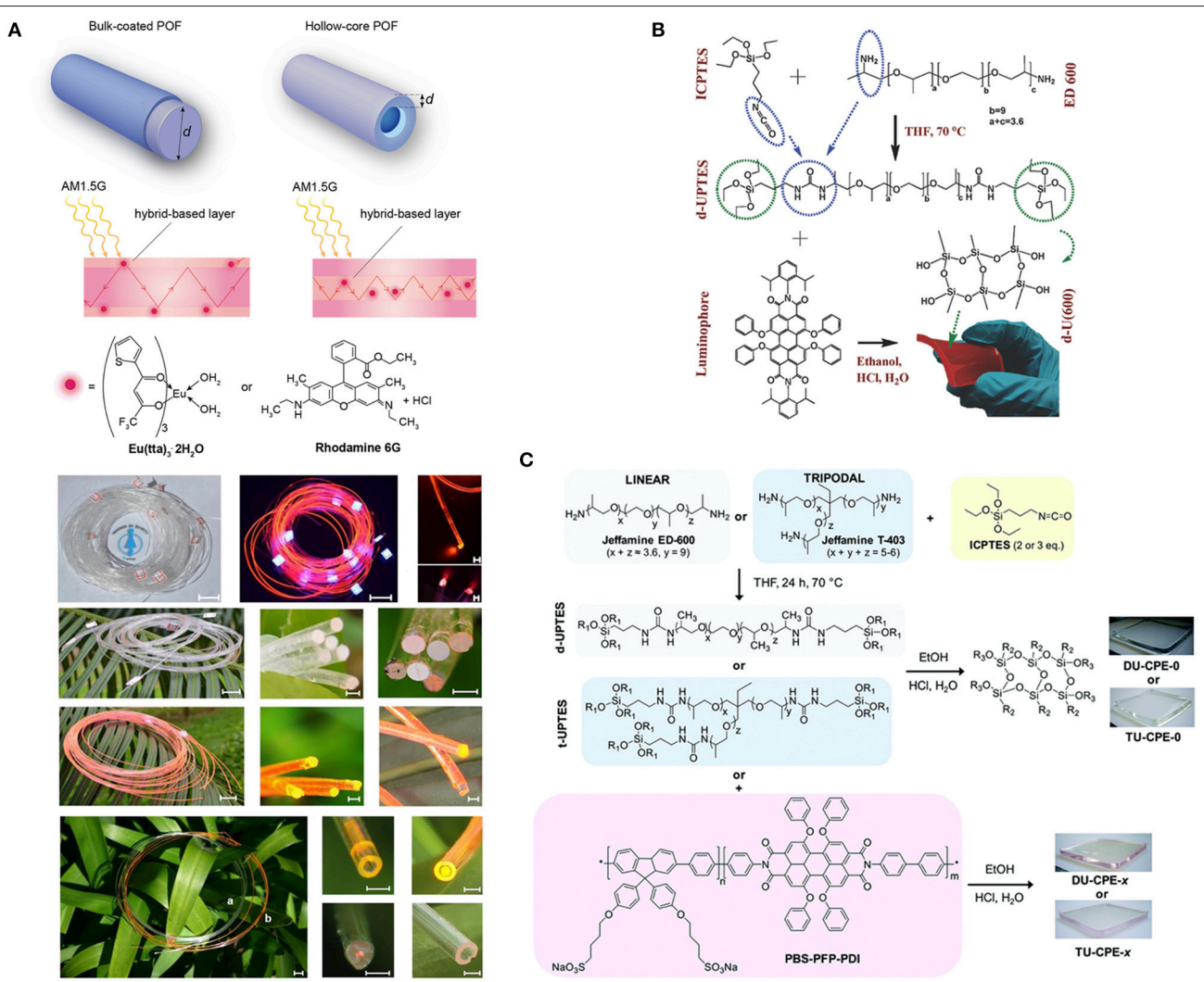

FIGURE 1 | (A) Schematic representation of optical fiber LSCs with the used luminescent active layers and corresponding photographs of the obtained demonstrators. Adapted with permission from Correia et al. (2016). Copyright 2016, John and Wiley and Sons. **(B)** Schematic representation of the chemical mechanism for the formation of planar di-ureasil LSCs doped with LR305. Reproduced with permission from Kaniyoor et al. (2016). Copyright 2015, WILEY–VCH Verlag GmbH & Co. KGaA. **(C)** Synthetic route for the preparation of ureasil-based LSCs embedding a conjugated polyelectrolyte as luminophore. Reproduced with permission from Meazzini et al. (2017). Copyright 2017, The Royal Society of Chemistry.

the guest fluorophore (LR305) were deposited simultaneously from the solid state on the target substrate (glass or PMMA), thereby allowing the *in-situ* formation of a parylene polymeric film embedding a fine dispersion of the dye within the matrix, while maintaining its surface roughness in the nanometer range. Tests on LSCs obtained by depositing fluorescent parylene films on glass and polymer waveguides showed a maximum η_{opt} as high as 22.6%. Further studies by the same group focused on widening the applicability of vacuum-deposited parylene-based matrices in combination with another luminescent species based on the rare-earth complex tris(2-thenoyl trifluoroacetone) mono (1,10-phenantroline) europium (III) ($Eu(tta)_3phen$) (Tonezzer et al., 2015).

The increasing demand for environmentally-friendly materials has recently led to the development of novel bio-based polymeric host matrices that may offer some ecological advantages compared with conventional oil-based systems. Within this framework, a poly-L-lactic acid (PLA) matrix was proposed as an environmentally friendly alternative to PMMA in LSC applications (Fattori et al., 2011). The smaller index of refraction of PLA *vs.* PMMA led to a minor reduction in maximum light trapped. On the other hand, when a luminescent species was added to the PLA matrix, the PLQY resulted to be higher than in PMMA at similar loading. Further studies from the same research group reported on another class of biopolymer-based eco-friendly matrix from silk fibroin (SF) (Melucci et al., 2012), with promising optical properties.

Another potential source of useful bio-based materials is represented by lignocellulosic biomass, in which cellulose is present as major constituent (Tuck et al., 2012). The possibility to exploit cellulose nanocrystals (CNCs) as host matrix in thin-film LSCs was recently assessed in comparison to a more conventional

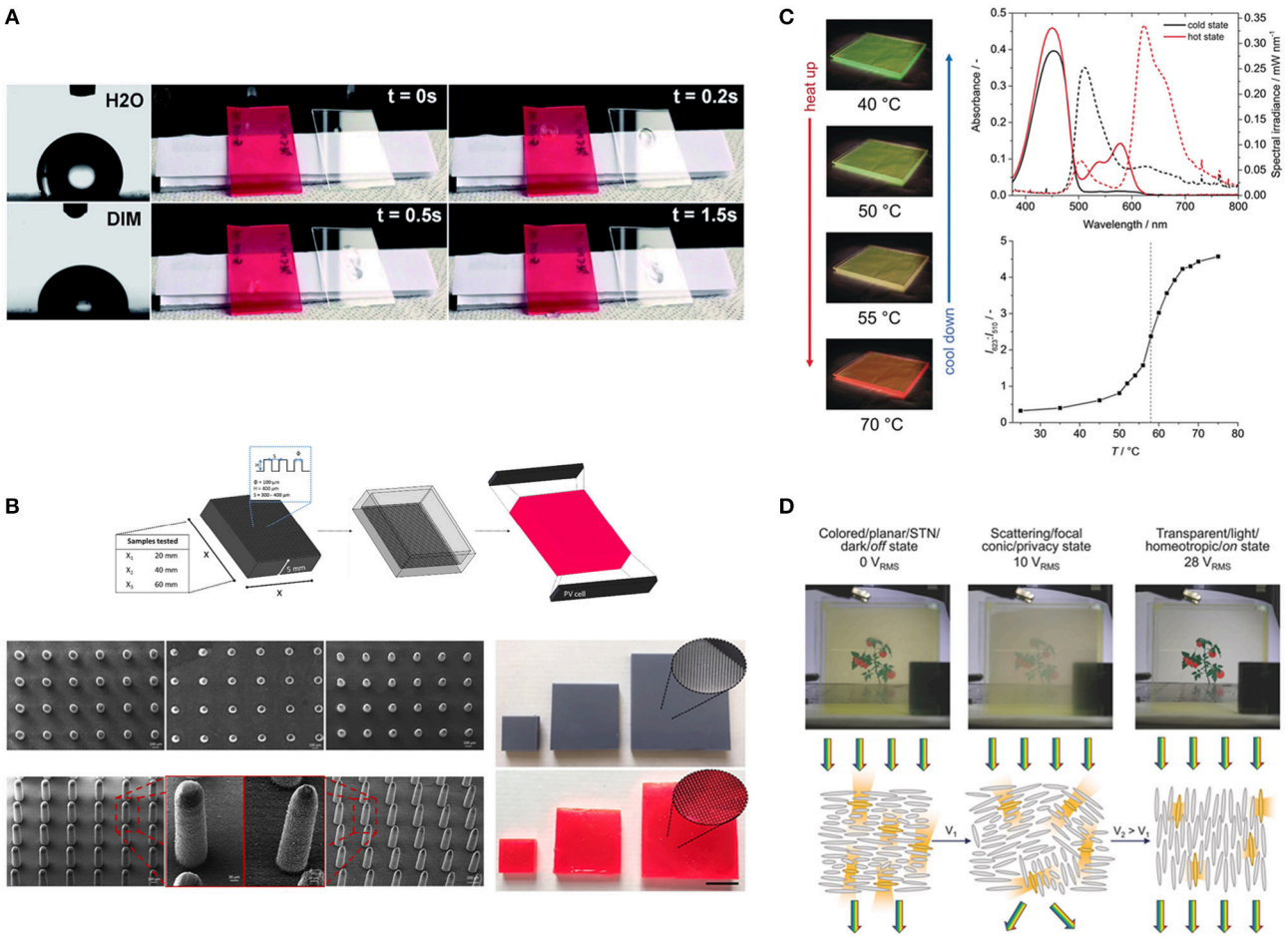

FIGURE 2 | (A) Surface wettability behavior of fluorinated LSCs compared with bare glass as observed from movie stills depicting water droplets falling at increasing times. Adapted with permission from Pintossi et al. (2017). Copyright 2017, The Royal Society of Chemistry. **(B)** Scheme illustrating the fabrication process to realize superhydrophobic LSCs, SEM images of the obtained surface features and photographs of 3D-printed templates (Upper) with corresponding LSCs devices (Lower) obtained by replica molding. Adapted with permission from Credi et al. (2017). Copyright 2017, Elsevier. **(C)** Photographs of a thermo-responsive LSC demonstrating the color change as the surrounding temperature is increased from 40 to 70°C, with changes in the optical response measured in terms of absorbance spectrum, edge emission spectrum, and ratio between edge emission intensities at 623 and 510 nm. Adapted with permission from Sol et al. (2018a) under the terms of the CC BY-NC license. **(D)** Photographs of the smart LSC window at increasing bias with a schematic representation of LCs and dyes alignment, and the emission direction. Adapted with permission from Sol et al. (2018b). Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA.

acrylic polymer emulsion, in both cases using rhodamine 6G as fluorescent doping species (Chowdhury et al., 2017). It was shown that the CNC matrix may be considered suitable as host matrix material because of the enhanced absorption properties compared to the acrylic polymer emulsion. However, the latter behaved better as waveguide maintaining high efficiency also for long light propagating distances.

Very recently (Geervliet et al., 2018), two different types of renewable polyesters obtained *via* a catalyzed two-step melt-polycondensation reaction (a homopolymer of diethyl 2,3:4,5-di-*O*-methylene galactarate (GxMe) and isosorbide and a random copolymer of GxMe with 1,3-propanediol and dimethyl terephthalate) were proposed as host matrix materials in thin film LSCs. The spectroscopic characterization and the η_{opt} of resulting LSCs (embedding LR305 or an aggregation-induced emission molecule as guest luminophores) evidenced a performance similar or superior to that of reference LSC thin films based on PMMA/LR305, thus further indicating the potential of bio-based polymers as valuable renewable matrices for high-performance LSCs.

ORGANIC-INORGANIC HYBRID MATRICES

In addition to purely polymeric materials, also hybrid organic-inorganic systems have been thoroughly investigated as viable option for LSC host matrices. In these materials the high refractive index and enhanced stability typical of inorganic glasses are combined with the good processability and accessible chemical functionality characteristic of polymers (Pandey and Mishra, 2011; Reisfeld et al., 2011).

An interesting demonstration of LSCs based on a hybrid system employed a polysiloxane-rubber waveguide as flexible host material for LSC applications doped with LR305 (Buffa et al., 2012). It was shown that for low dye concentrations efficiencies comparable to those obtained by using conventional PC waveguides could be achieved, as a result of the good dispersibility of the fluorophore in these conditions. On the contrary, at higher concentrations luminescence quenching was observed, associated to the lower solubility of the luminophore in an apolar environment. LSC devices obtained by coupling this doped polysiloxane rubber with Si or GaAs PV cells demonstrated the viability of this material as flexible host matrix system for LSCs.

In the field of glassy hybrids, bridged silsesquioxanes containing europium(III) salts and 2-thenoyltrifluoroacetone were more recently proposed as integrated host-guest system for LSC device applications (Freitas et al., 2015). It was shown that high η_{opt} could be reached due to the peculiar optical properties resulting from the combination of the Eu^{3+} complex and the hybrid matrix. This allowed the easy fabrication of free-standing thick films (440 μm) and highly luminescent coatings (200–400 nm) on glass substrates exhibiting acceptable PLQY (∼60%). Further studies concentrated on the use of different functional bridged silsesquioxanes in combination with various trivalent lanthanide ions (Ln^{3+}), demonstrating the high versatility of these systems for the production of defect- and crack-free films with controlled nanostructure *via* the sol-gel chemistry (Graffion et al., 2011, 2012).

Another important class of sol-gel-based hybrid materials widely investigated as host matrices for LSCs is that of ureasil systems. These compounds are generally prepared from the reaction between a commercially available polyetheramine and an organo-silica precursor, followed by hydrolysis and condensation of the silica network using sol-gel chemistry (McKenna and Evans, 2017). One interesting application based on such ureasil matrices is their use to fabricate cylindrical LSCs. In a first proof of concept study, a commercial PMMA optical fiber was coated with an organic-inorganic ureasil hybrid layer doped with a Eu^{3+} complex as luminescent species (Correia et al., 2015). Optimized fiber-based LSC devices could attain $\eta_{opt} > 20\%$, calculated in the absorption spectral region of the luminescent material (300–380 nm). Using an optical-fiber drawing facility, the same group extended their previous studies by scaling up large-area LSCs (up to 2.5 m) based on bulk and hollow-core optical fibers (**Figure 1A**), using rhodamine 6G- or Eu^{3+}-doped hybrids based on two different matrices, namely a di-ureasil and a tripodal tri-ureasil system (Correia et al., 2016). Efforts on the use of tri- and di-ureasil compounds as host matrices in LSCs have also focused on their combination with different doping species in planar devices (Nolasco et al., 2013; Rondão et al., 2017; Frias et al., 2018).

The ureasil family was recently further exploited as precursor for the formation of host matrix systems for planar LSC devices in bulk configuration and embedding LR305 as luminescent species (Kaniyoor et al., 2016). The host matrix was obtained by the reaction between a polyetheramine of the Jeffamine family and an isocyanate-functionalized organo-silane with the formation of urea bonds (**Figure 1B**). From the optical analysis it was found that this material exhibits enhanced transmittance in the whole UV-visible range, with optical clarity (and refractive index) comparable to glass or PMMA. Förster resonance energy transfer (FRET) was demonstrated between the matrix and the organic dye, which enabled an extension of the light-harvesting window of the LSC device. For optimized devices, $\eta_{opt} = 14.5\%$ (emission: 300–800 nm, $G = 3.3$) was reported. In a later work (Meazzini et al., 2017), the same class of host matrix system was tested in the presence of a poly(fluorene-*alt*-phenylene) copolymer containing on-chain perylenediimide chromophore units as the luminophore (**Figure 1C**), further confirming the key role played by the interplay between host matrix material and guest luminescent species in determining the optical performance of the resulting LSC.

MULTIFUNCTIONAL MATRICES

Recent efforts in the field of LSCs have been addressed to the development of multifunctional systems in which the matrix material not only acts as host environment for the luminophore, but also displays added functionalities such as extended photochemical durability, peculiar surface properties and/or stimuli-responsiveness. Within this context

(Pintossi et al., 2017), a novel photopolymeric matrix for thin-film LSCs was recently developed for higher outdoor durability but also displaying a highly hydrophobic and oleophobic surface character (**Figure 2A**). Such system was based on a blend of three different UV-curable fluorinated oligomers to be co-reacted upon UV-light exposure with a suitably functionalized perylene-based organic luminophore bearing lateral carbon double bonds, to yield a solid crosslinked LSC thin film. The long-term stability of such photocurable LSC system was demonstrated by full retention of its initial performance, as opposed to the decline observed in reference host/guest luminescent systems. The highly hydrophobic character (water contact angle $\sim$120°) and moderate oleophobicity (mineral-oil contact angle $>$ 90°) resulting from the highly perfluorinated nature of the polymeric matrix was shown to impart easy cleanability to the LSC coating. In a successive work by the same group, superhydrophobicity of the LSC surface could be achieved by combining a soft-lithographic process together with an additive manufacturing approach based on stereolithography (Credi et al., 2017). Surface-microstructured superhydrophobic LSCs could be obtained using a suitably developed UV-curable formulation incorporating perfluorinated monomers doped with LR305 (**Figure 2B**), leading to water contact angles $>$160°.

Another interesting approach to multifunctionality in LSCs is focused on providing the host matrix with thermo-responsive properties. In this respect, the possibility to have liquid crystals (LC) as host matrix was recently explored, with the incorporation of donor–acceptor fluorescent dye pairs which could yield fluorescence through a FRET mechanism (Sol et al., 2018a). In particular, at low temperature one of the two dyes is in its aggregated form, preventing any type of fluorescence, while the second is emitting in the green region of the electromagnetic spectrum. Upon increasing temperature, the solubility of both dyes in the LC matrix increases and FRET phenomena are allowed to occur, shifting the emission of the device from green toward red. This system (**Figure 2C**) offers the opportunity to tune both absorption and emission colors, which may be a particularly interesting esthetic feature with great potential for LSCs and smart windows in general. Furthermore, positive and negative dichroic dyes can be exploited to change the appearance of a window as a function of applied voltage (**Figure 2D**) (Verbunt et al., 2009; Debije et al., 2014; Khandelwal et al., 2015; Sol et al., 2018b).

CONCLUSIONS AND PERSPECTIVES

The importance of the selection of appropriate host matrix materials for LSCs has driven research to the development of novel systems working alongside more conventional host matrix platforms such as glass or commodity polymers. Within this framework, the extensive array of properties achievable by the use of polymers has made them the most widely exploited class of materials for use in LSC devices. Together with polymers, research has also focused on the development of hybrid systems to simultaneously exploit the beneficial properties of both the glassy inorganic phase (chemical inertness, optical clarity) and the organic phase (chemical tunability, light-weight). Only recently, the attention has been also shifted toward matrix materials capable of imparting added functionalities to the LSC ensemble. In this respect, examples of (super)hydrophobic, oleophobic, or stimuli (thermally, electrically) responsive host matrices have been proposed and successfully demonstrated.

Considering that research on alternative matrix materials for LSCs has been addressed in detail only in recent years, the examples presented in this mini-review clearly demonstrate that there are enormous opportunities for enhanced LSC performance by developing suitably tailored host materials. In addition, the development of multifunctional matrix systems will be expected to pave the path to novel and truly smart devices with potential application in a variety of fields, thus anticipating a wider permeation of the LSC technology into the market.

AUTHOR CONTRIBUTIONS

The author confirms being the sole contributor of this work and has approved it for publication.

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