Preventing UV-light damage of light sensitive materials using a highly protective UV-absorbing coating

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One of the most important drawbacks of classical and new advanced functional materials for applications outdoors, or in environments with high UV irradiation, is the light induced damage that reduces drastically their effective operation lifetime or durability. This makes protecting light sensitive materials against UV irradiation a nowadays important technological demand in almost every industrial field. This *tutorial review* incorporates the main aspects of UV damage to materials and describes the recently developed highly effective thin UV-protective coatings, based on UV-absorber molecules entrapped in a Sol–Gel derived ormosil matrix.

1. Introduction

UV light, natural or artificial, is responsible for the decomposition and degradation of organic compounds, the discoloration of dyes and pigments and the loss of mechanical properties and gloss in polymers and plastics. Most modern commonly used articles and devices are fabricated, to a certain extent, with polymers or organic matter. Many efforts have been devoted to reduce the damage to these materials and improve their durability upon exposure to UV light. The results, however, have been only moderately successful. A simple search in Google reveals more than 12 million entries dealing with UV and degradation or damage, showing the great importance of this issue in different application fields.

We have recently developed an organically modified silica (*ormosil*) coating doped with highly efficient UV-absorber molecules, that effectively prevents the UV light from reaching

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David Levy began in 1982 pioneering the first application of the sol–gel process for preparation of "organically-doped silica gel-glasses". He was awarded the "First Ulrich Prize" (1991), and was nominated by CSIC for the "Juan Carlos-I Rey award. He has authored over 110 papers, reviews, book chapters and patents on optical Sol–Gel materials. His research interest is optically active/photoactive/electroactive materials (bulk, thin-film and nanoparticles) and liquid crystal materials by Sol–Gel processing and their applications. He is a member of the Organizing Program Committees of the "International Workshops on Sol–Gel Science and Technology", "Sol–Gel Optics" of the SPIE, and participated at the EU Experts Panel of the GROWTH Materials Research Programme. DL heads the Sol–Gel Group at ICMM, and is Research Professor at ICMM-CSIC, and headed for 10 years the LINES at the National Institute of Aerospace Technology.

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Marcos Zayat received his PhD degree in Chemistry from the Hebrew University of Jerusalem, Israel in 1997, under the supervision of Prof. Renata Reisfeld. He is currently a research fellow (Ramon y Cajal Program) in the Materials Science Institute of Madrid (ICMM-CSIC) and the Autonomous University of Madrid (UAM). His main research interests are the development of new Sol–Gel prepared materials for optical and electro-optical applications: thin-films, mixed oxides nanoparticles and pigments.

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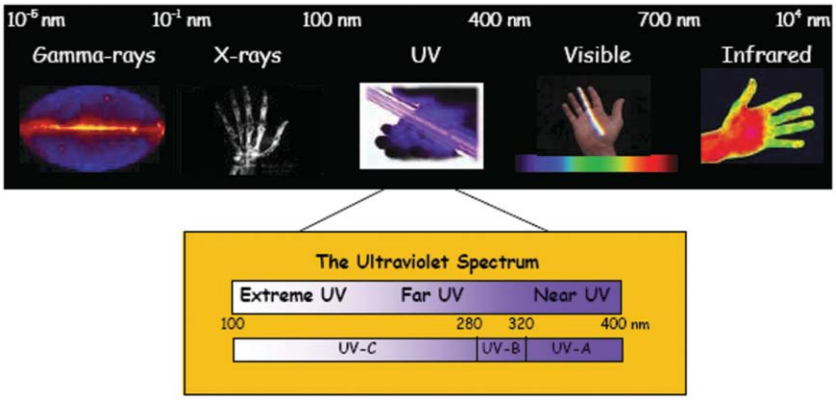

Fig. 1 UV light.

the protected substrate-surface.[1,2] The resulting submicrometric coatings are fully transparent in the visible part of the spectrum, and do not affect the colour or the optical properties of the substrates to be protected. Moreover, the highly photostable coatings are applied and cured at room temperature, extending the wide range of possible applications of the protective coatings to heat sensitive materials.

2. Ultraviolet radiation

Ultraviolet radiation, sometimes called ultraviolet light, is invisible electromagnetic radiation of the same nature as visible light, but having shorter wavelengths and higher energies. In the electromagnetic spectrum, UV radiation extends between the blue end of the visible spectrum (400 nm) and low-energy X-rays, straddling the boundary between ionizing and non-ionizing radiation, which is conventionally set at 100 nm (Fig. 1).

UV radiation is conventionally classified into 3 bands in order of increasing energy: UV-A (320–400 nm), UV-B (280–320 nm) and UV-C (100–280 nm). This division was put forward by the Commission Interntionale de l'Eclairage (CIE), and corresponds broadly to the effects of UV radiation on biological tissue.

2.1. Main sources of ultraviolet radiation

The main source of natural ultraviolet radiation is the sun. About 1000 W m^{-2} of the incident solar irradiation reaches the Earth's surface without being significantly scattered. Most of this radiation is infrared light (55%) and visible light (40%), and approximately 5% of the ground-level solar radiation is ultraviolet radiation, mostly in the UV-A range. The terrestrial solar spectrum is shown in Fig. 2.

Solar UV radiation varies strongly with season, time of day, latitude and atmospheric conditions, generally reaching a daily peak around solar noon and a yearly peak in summer (Fig. 3). UV-B levels change rapidly with time of day while UV-A levels vary more slowly throughout the day. UV-B radiation is strongly absorbed by stratospheric ozone and small changes in the protective ozone layer can produce large increases in UV-B radiation reaching the Earth's surface (Fig. 4). Solar UV-C radiation does not reach the Earth's surface because it is absorbed by ozone and other gases in the atmosphere.

In addition to solar UV radiation, there are a variety of artificial sources of UV light. These sources are widely used in some occupational, medical, and recreational settings. The most common artificial sources of UV radiation are arc-lamps, and fluorescent or incandescent lighting.

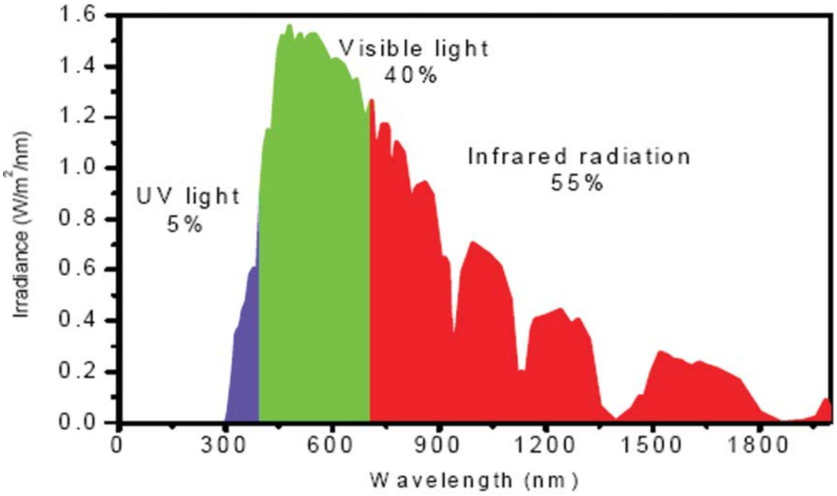

Fig. 2 Solar spectrum reaching the Earth's surface after being filtered by the different gases in the atmosphere.

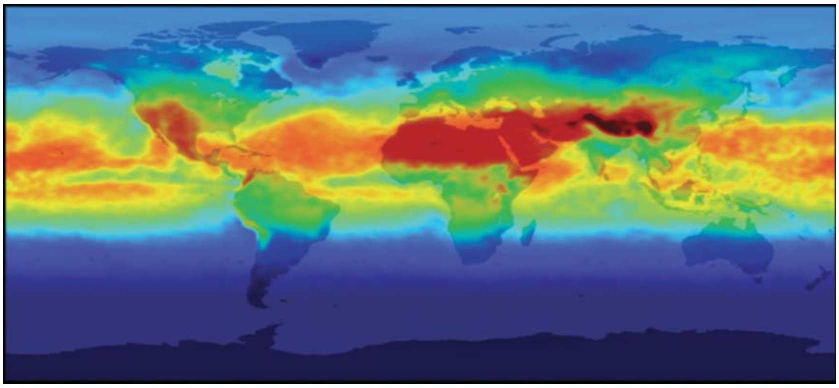

Fig. 3 Global plot of UV levels in July—dark brown being the highest (NASA/Goddard Space Flight Center, Scientific Visualization Studio).

Arc lamps emit in a wide range of wavelengths including a large amount of UV-A and UV-B and some UV-C light. Short arc lamps are usually used in movie theatre projectors, searchlights, specialized medical equipment with fibre-optic light delivery means, some stage spotlights ("followspots"), in some scientific equipment or when an extremely intense light source is required. Mercury, mercury–xenon, deuterium and metal halide short arc lamps emit large amounts of UV light and are the most common sources for artificial UV radiation.

Tungsten halogen incandescent lamps emit a significant amount of UV light. Fluorescent and incandescent lighting are widely used but do not emit significant amounts of UV radiation under normal use. Fluorescent lamps produce UV radiation by ionizing low pressure mercury vapours. This radiation is absorbed by a phosphor coating on the inside of the tube that converts it to visible light. Some UV radiation may leak through the phosphor coating, but the levels are generally low.

2.2. Other sources of UV light

Electric welding arcs are strong sources of ultraviolet radiation; they can produce acute exposure to UV radiation within a radius of several meters in just a few seconds. Germicidal lamps, commonly used for sterilization in hospitals, are also strong emitters of UV-B and UV-C radiation. Curing lamps use UV radiation to harden resins and to dry paints and other substances. They can be quite intense, but are usually located inside enclosed cabinets. Therapeutic UV radiation lamps, used in physiotherapy and dermatology for the treatment of psoriasis and other skin conditions can emit either UV-A or UV-B. "Black lights" are low intensity UV-A lamps used for non-destructive testing, insect control, and in the entertainment industry. Ultraviolet lasers are used for medical and industrial applications. They emit intense UV radiation at a single wavelength so, unlike most other UV-radiation sources, they emit no visible light.

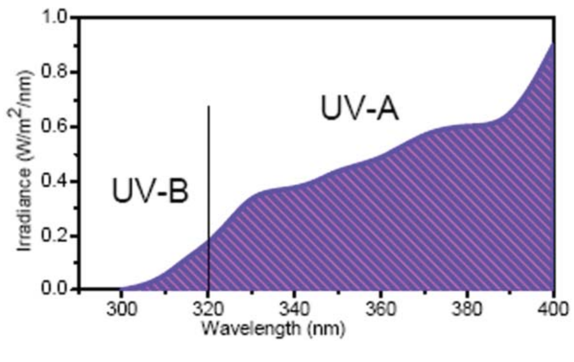

Fig. 4 Terrestrial solar UV radiation.

3. What are the effects of UV light on materials?

Common organic materials, such as most plastics, polymers, wood, *etc.*, absorb ultraviolet radiation and undergo a rapid photolytic and photo-oxidative reaction that results in their photodegradation.[3] The damage to organic materials by UV light is a well known issue. The energy of the photons in the ultraviolet region (290–400 nm) is sufficient to break chemical bonds in polymers, wood, paper and other organic based materials, resulting in the formation of free radicals.[4]

A photochemical reaction occurs as a result of activation of a molecule or polymer by light to its excited singlet (S*) and/or triplet (T*) states. Pure degradation, consisting of chain scission and crosslinking, occurs only in inert atmosphere, however, in the presence of air, polymers and other organic materials undergo a photo-oxidative degradation. The degradation of these materials can be described as follows: The free radicals produced by the effect of UV light react with other molecules of the polymer to form oxy and peroxy radicals, resulting in chain scission. The reaction continues until two free radical react with each other, forming stable non-radical compounds. The main reactions occurring during the photodegradation of polymers are given in Table 1.

The loss of strength, impact resistance, and mechanical integrity of polymers exposed to UV light is well known. These changes in mechanical properties reflect polymer chain scission

Table 1 Main reactions of the photo oxidative degradation of polymers

Initiation (UV light)	$\mathrm{R{-}H \rightarrow R^{\bullet} + H^{\bullet}}$
Propagation	$\mathrm{R^{\bullet} + O_2 \rightarrow R{-}O{-}O^{\bullet}}$
	$\mathrm{R{-}O{-}O^{\bullet} + R{-}H \rightarrow R{-}O{-}OH + R^{\bullet}}$
	$\mathrm{R{-}O{-}OH \rightarrow R{-}O^{\bullet} + OH^{\bullet}}$
Termination	$\mathrm{R^{\bullet} + R^{\bullet} \rightarrow R{-}R}$
	$\mathrm{R^{\bullet} + R{-}O{-}O^{\bullet} \rightarrow R{-}O{-}O{-}R}$
	$\mathrm{R{-}O{-}O^{\bullet} + R{-}O{-}O^{\bullet} \rightarrow}$ $\mathrm{R{-}O{-}O{-}R}$ + nonradical products

Fig. 5 Wood samples before (left) and after degradation with UV light.

as a result of photodegradation. At the same time, polymers progressively lose their coloration and acquire a yellowish tint after prolonged exposure to UV light.[3,5]

Ultraviolet light is the main factor responsible for the degradation of wood, as it initiates a range of chemical reactions at the wood surface, that result in the roughening and change in colour of the surface, wood checking (fracturing) and finally cracking. The vulnerability to weathering in wood is strongly related to the relative amount of cellulose, hemicellulose and lignin in its composition, the latter being the most sensitive to photodegradation.[6,7] Fig. 5 shows a piece of wood darkened by the effects of UV light.

Artwork in museums suffers an important photodegradation, as art pieces are exposed for large periods of time to natural and artificial illumination.[8] The dyes in paintings and photographs undergo a progressive fading, finally losing their coloration. UV radiation is especially harmful to libraries and archival materials as it leads to the weakening and embrittlement of cellulose fibres and causes paper to bleach, yellow or darken, depending upon its constituents (Fig. 6).

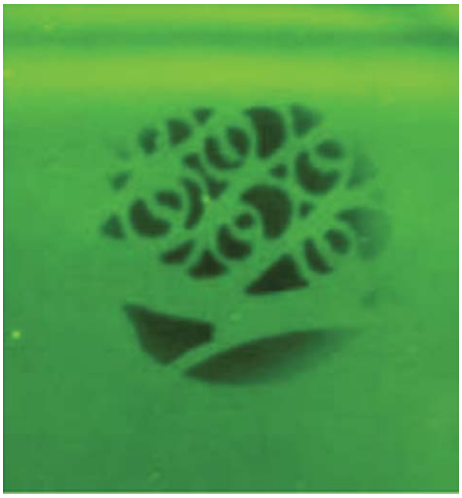

Fig. 7 Fluorescent coating exposed to intense UV radiation through a metallic mask. Dark zones were damaged by the UV radiation.

The automotive industry employs a large number of plastic parts in a car, which are exposed for very long periods of time to direct solar radiation. This includes also the parts which are inside the car, being exposed to UV radiation through the windows and windshields. There is a great interest in protecting these materials as well as to reducing the exposure of the occupants of cars to UV light.[9,10]

In Space, the degradation of materials by UV light is much more pronounced than on the Earth's surface, due to the important filtering properties of the gases in the atmosphere. Therefore, materials designed for Space applications must be protected to avoid or reduce the deleterious effect of UV radiation.[11]

Advanced optical devices very often include materials and compounds susceptible to degradation when exposed to UV light. Different parts, such as filters, coatings, *etc.* need to be protected in order to avoid or reduce their degradation.

UV light can cause important damage to human tissue. UV-C can damage DNA and other molecules and is often used as a germicidal agent. Exposure to both, UV-B and UV-A leads to tanning and sunburn (erythema), and can affect the immune system. UV-A penetrates deeper into the skin due to its longer wavelength and plays a role in skin photoaging. Tanning lamps emit mostly UV-A radiation with a few percent content of UV-B.

Fig. 6 Examples of materials susceptible to degradation by UV light: Paintings (left), paper darkening (center) and dye discoloration in books (right).

4. Protection of materials against UV radiation

There are different methods to protect matter from the harmful effects of UV radiation. One of the most widely used methods in industry is the dispersion of UV-absorbing agents in the photodegradable material, reducing its degradation upon exposure to UV light. There are inorganic and organic materials that can be used to protect against UV radiation. Inorganic materials are based mainly on mixed oxide films or particles, able to absorb or scatter light. On the other hand, there are several organic molecules which efficiently absorb UV light, and can also be used for this purpose.

The possibility of coating the photosensitive materials with a UV-absorbing film was studied extensively for inorganic and polymer based coatings. The inorganic coatings, however, were limited in application to heat resistant substrates, due to the high curing temperature required to obtain the protective coating. On the other hand, dispersions of UV-absorbing molecules in polymer matrices exhibit low photostability upon prolonged irradiation with UV light, as the matrix itself is degraded during irradiation.

4.1. Inorganic UV-absorbing systems

Many inorganic UV-absorbing systems based on particles or thin film coatings have been developed. Inorganic oxides such as TiO_2, CeO_2 and ZnO are the most widely used for protection against UV radiation.[13–19] The attenuation of the UV radiation in these materials is accomplished by both, bandgap absorption and scattering of light.[12] The UV light is strongly absorbed by excitation of electrons from the valence band to the conduction band. TiO_2 and ZnO have bandgap energies corresponding to wavelengths of 365 nm and 380 nm, respectively. Light below these wavelengths has sufficient energy to excite electrons and hence is absorbed by TiO_2 and ZnO. Light having a wavelength longer than the band gap wavelength will not be absorbed. The intensity of scattered light is a function of particle size as well as the refractive indices of the particles and the media. Through careful control of particle size a maximum scattering of UV light can be obtained, meanwhile the scattering of visible light must be eliminated to obtain high transparency. Mixed CeO_2–TiO_2 films were shown to be an efficient UV-absorber, however, they exhibit a slight yellow coloration due to the tail of the absorption peak that enters the visible range of the spectrum.[13,14] Nanoparticles of TiO_2, SiO_2 coated TiO_2 and ZnO, are used as UV absorbers in sunscreen cosmetics.[15–19] Hybrid organic–inorganic matrices have also been used to disperse inorganic UV-absorbers in thin films.[20]

4.2. Highly efficient organic UV-absorber (UVA) molecules

UV absorbers have been used in order to reduce the damaging effects of the UV radiation and achieve an adequate conservation of the properties of the materials. The UV absorbers must be colourless or nearly colourless compounds having high absorption coefficients in the UV range of the spectrum. In order to offer an effective protection against UV radiation the UV-absorber molecules must transform the absorbed energy into less harmful energy before reaching the substrate and exhibit good photostability.

One the most important families of UV-absorber molecules include a phenolic group that plays an important role in the dissipation of the absorbed energy. Phenolic-type UV absorbers involve compounds forming O–H–O bridges, such as salicylates, 2-hydroxybenzophenones, 2,2′-dihydroxybenzophenones, 3-hydroxyflavones or xantones and compounds forming O–H–N bridges, such as 2-(2-hydroxyphenyl)benzotriazoles and 2-(2-hydroxyphenyl)-1,3,5-triazines. The structures of these compounds are shown in Fig. 8.

These UV absorbers with an intramolecular hydrogen bond possess an efficient radiationless mechanism of energy dissipation: Excited State Intramolecular Proton Transfer (ESIPT).[21–26] The ESIPT mechanism is illustrated in Fig. 9.

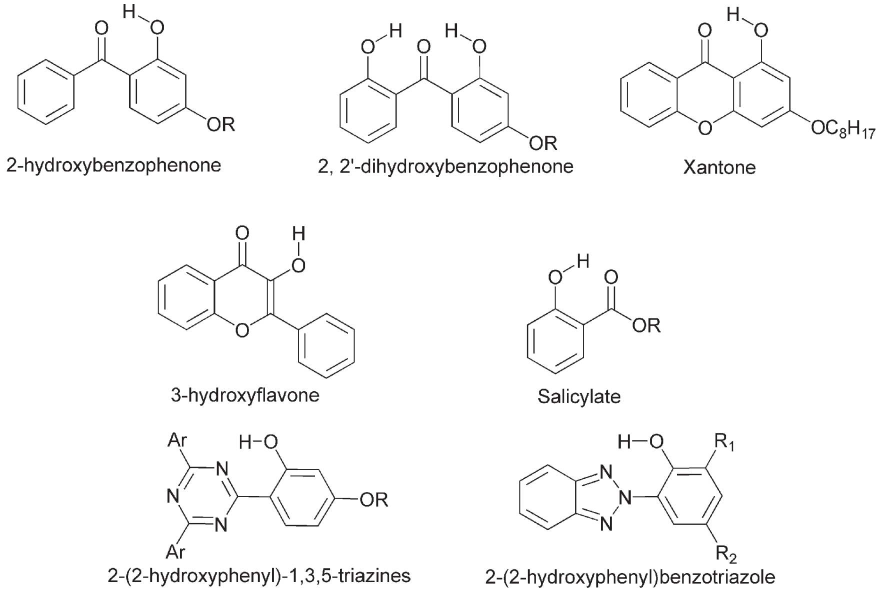

Fig. 8 Chemical structures of phenolic UV-absorbers.

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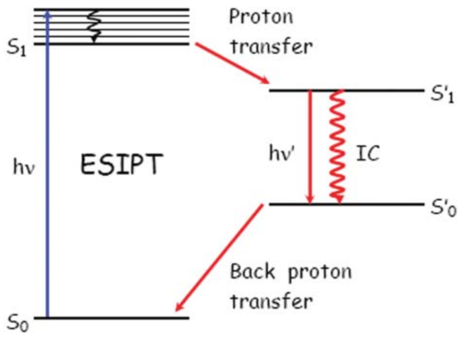

Fig. 9 ESIPT mechanism of energy dissipation.

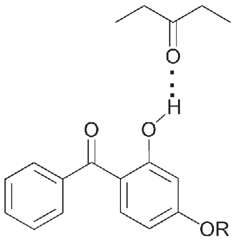

Fig. 10 Disruption of the intramolecular H-bond in a benzophenone derivative and the formation of an intermolecular H-bond with a polar group of the matrix.

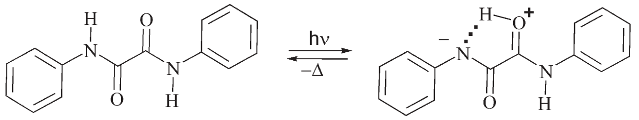

Fig. 12 Energy dissipation mechanism of oxanilide.

The UV-absorbers molecules contain acid and basic groups in a reasonably close proximity, and in accordance with Förster theory[27,29] show a pronounced difference between excited state and ground state acidity of about 7 pK_a units, due to changes in the electronic distribution. The acid group in the UVA molecule is the phenolic hydroxyl. The basic acceptor is the nitrogen atom in the heterocyclic or the oxygen atom in the carbonyl group. When the UV-absorber molecule is excited to the first singlet state (S_1), the increased acidity promotes a proton transfer to create a tautomeric species in its first excited singlet state (S'_1, Fig. 9). In most cases, the tautomeric species loses its energy by a non-radiative decay process as thermal energy. It should be noted that the contribution of this energy to the thermal degradation of the material is negligible compared to the much stronger thermal energy reaching the sample from the solar radiation. In some cases, (*e.g.*, 3-hydroxyflavones, salicylates and xantones) the dissipation of the energy from the tautomeric species is accomplished by a fluorescent emission with an unusually large Stokes shift.[28,29] Klöpffer[29] reported that certain derivatives of benzophenone may undergo a variety of mechanistic pathways of energy dissipation, after the excitation to S_1, including the formation of triplet states (T_1 and T'_1). A reverse proton transfer regenerates the ground state of the fundamental form of the UV absorber (S_0).

The ESIPT mechanism is responsible for the exceptionally high photostability of these molecules, due to the fact that the process occurs on an ultrafast picosecond timescale, which reduces the probability of chemical reactions in the excited state. Phenolic UVA molecules show very small quantum yields of photodecomposition in the 10^{-7} to 10^{-6} range.

The matrix, in which the organic UV-absorber is embedded, is the main factor affecting the stability of the molecule. Basic and polar matrices are capable of forming intermolecular H-bonds with the acid phenolic hydroxyl groups, disrupting the intramolecular H-bond and therefore preventing the ESIPT mechanism to take place.[21,30] This is usually accompanied by the appearance of fluorescence and increased photoreactivity. This issue can be observed in Fig. 10.

The ESIPT mechanism proceeds effectively only in planar five or six-membered rings, having an intramolecular hydrogen bond between the phenolic hydrogen and the heteroatom (nitrogen atom in benzotriazoles and triazines, and oxygen atom in salicylates, benzophenones, flavones or xantones).

In benzotriazoles, the formation of an intermolecular hydrogen bond with the matrix results in the loss of planarity due to the rotation of the phenolic ring around the N–C bond, resulting in the loss of photostability of the molecule (Fig. 11).

The most important non-phenolic UV absorbers are oxanilides and cyanoacrilates. The mechanism of energy dissipation in oxanilides[21,26] is believed to be similar to the ESIPT mechanism occurring in phenolic UVA molecules. The oxanilide involves a *trans*-planar geometry and presence of intramolecular H-bonds between carbonyl and imine groups, as shown in Fig. 12. The ESIPT process creates an excited tautomer (S'_1) capable of undergoing intramolecular conversion to S'_0 and reverting rapidly to the original oxanilide structure, dissipating the excitation energy by a non-radiative process. Owing to a very short lifetime of the first excited singlet state the oxanilides show a high photochemical stability.

Cyanoacrylates[21,26] are remarkably photostable molecules, considering the absence of an ESIPT mechanism for energy

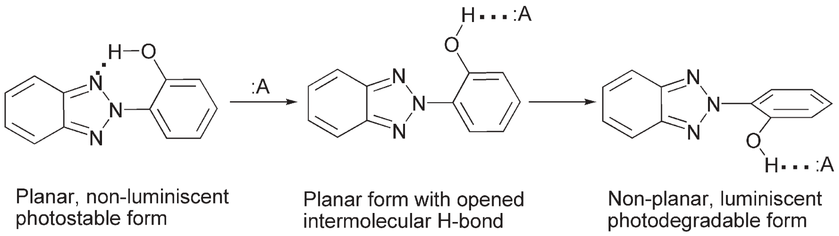

Fig. 11 Disruption of the intramolecular H-bond and loss of coplanarity in benzotriazoles in polar environments. :A = basic acceptor group.

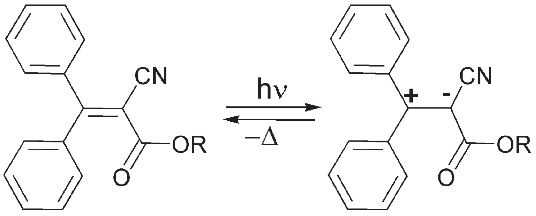

Fig. 13 Energy dissipation mechanism of cyanoacrylates.

dissipation. It seems likely that a charge-separated species could be formed from the excited state, allowing the dissipation of energy through rotation or increased vibration about the central bond (Fig. 13).

The UVA molecules can be incorporated in protective coatings to be applied on the photodegradable substrate. Alternatively, the molecules can be dispersed[31] or impregnated[32] in the same material that needs to be protected. Most of the coatings developed are based on dispersions of the UVA in polymeric matrices.[7,33,34] The incorporation of these molecules in inorganic matrices is limited by the heat treatment required for the formation of the matrix.

5. UV protective coatings based on dispersion of highly efficient UV-absorber molecules in Sol–Gel derived ormosil matrices

Recently developed highly efficient UV-protective coatings are based on a dispersion of a phenolic UV-absorber in a hybrid sol–gel matrix.[1] The resulting coatings allow incorporation of large amounts of UVA molecules, resulting in a strong absorption in the UV. In addition, the coatings present a very high stability upon prolonged exposure to UV light and are fully transparent in the visible region of the spectrum.

The highly efficient UV absorber, 2,2′-dihydroxy-4-methoxybenzophenone, was chosen for the preparation of these coatings, due to its very high photostability in non-polar environments. The sol–gel method allows the preparation of transparent, solid and porous inorganic matrices at low temperatures, and the incorporation of organic photoactive molecules in its porosity.[35,36] The method involves reactions of hydrolysis and condensation of silicon alkoxides (Fig. 14) to produce a 3-D, amorphous, porous and stable silica networks.

The Sol–Gel method allows the preparation of hybrid organic–inorganic matrices, by using organically modified alkoxide precursors. The non-hydrolysable organic groups of the alkoxide remain attached to the matrix porosity (Fig. 15). Employing these precursors allows the control of the polarity and size of the pores according to the nature and amount of the non-hydrolysable organic group used, as shown in Fig. 16 for a Sol–Gel coating on a transparent glass substrate.

Alkoxides modified with non-hydrolysable phenyl groups were used for the preparation of phenyl modified ormosil matrices for the entrapment of the UV-absorber molecules. The preparation and deposition of the UV-protective coatings by the spin-coating technique is described in Fig. 17.

Using phenyl groups to modify the silica matrix has important advantages for the preparation of the UV protective coatings. The phenyl modified matrices allow the introduction of large amounts of UVA molecules, resulting in strong

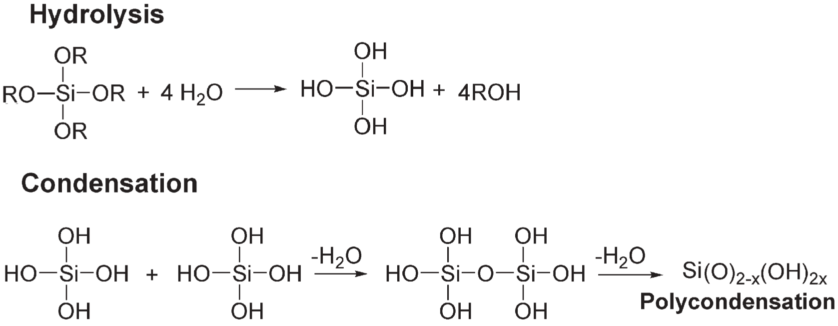

Fig. 14 Sol–Gel reactions to amorphous silica matrices.

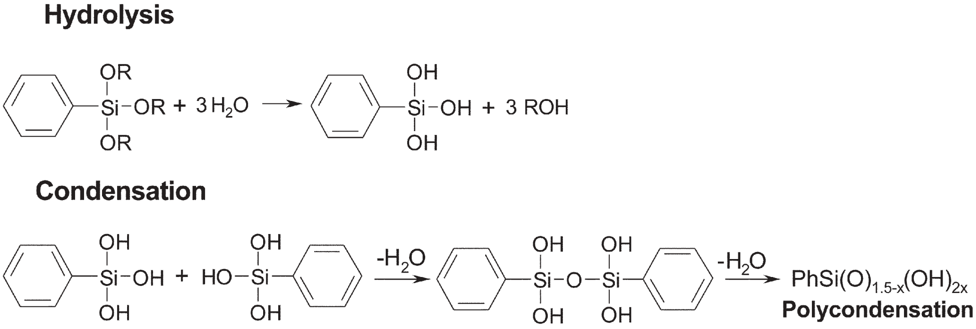

Fig. 15 Sol–Gel reactions of phenyl-modified alkoxide precursors.

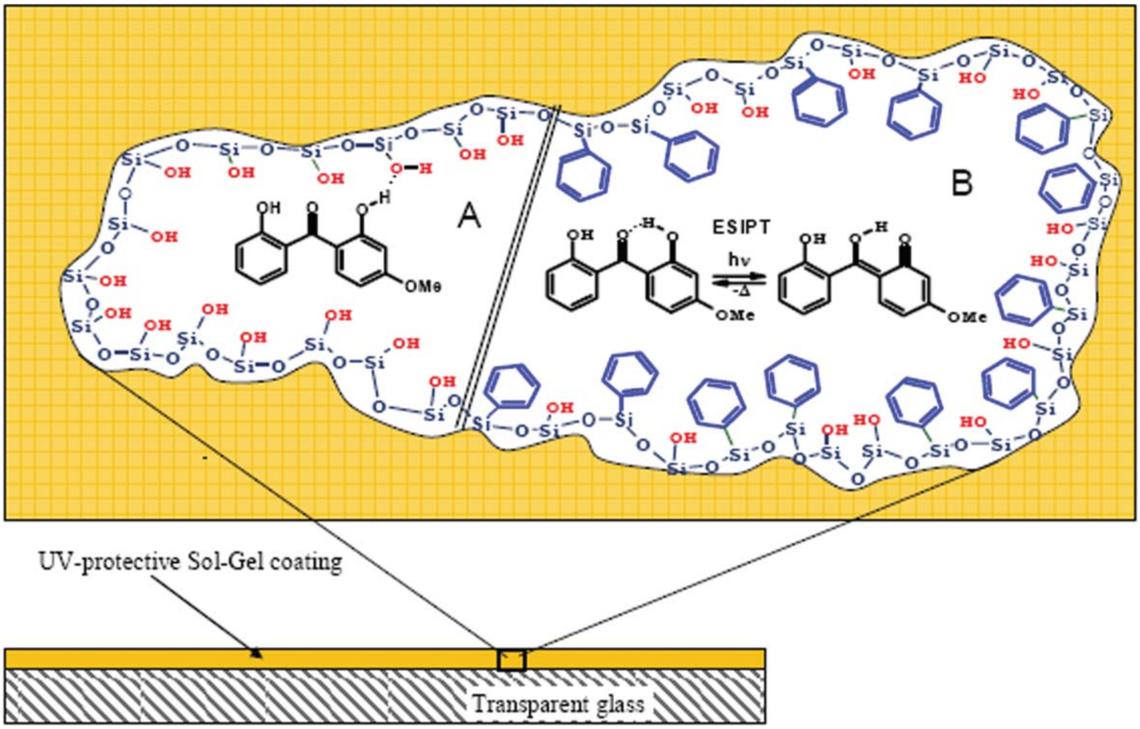

Fig. 16 UV-protective Sol–Gel coating: Schematic representation of the UV-absorber molecule in a silica matrix, where the polar OH groups at the surface of the pore disrupt the ESIPT mechanism (A) and the UVA molecule in a phenyl modified ormosil matrix, which allows the ESIPT mechanism to take place (B).

absorption in the UV range. In addition, the phenyl groups in the matrix screen the strongly polar silanol groups (≡Si–OH) of the surface of the pores, avoiding the disruption of the intramolecular hydrogen bond of the UV absorber allowing the ESIPT energy dissipation process to take place.

Another advantage of using these matrices to entrap the UVA molecules is the low temperature required for the drying and curing process of these films, which extend their potential application to heat sensitive substrates, such as those containing polymeric or organic materials.

The phenyl modified Sol–Gel matrices, due to their predominantly inorganic nature, exhibit high photostability upon irradiation with UV light. On the other hand, the use of polymeric matrices for the dispersion of the UV absorbers is limited by the low stability of the polymer upon UV irradiation. The free radicals generated in the photodecomposition of the polymers can react with the active form of the absorber molecules, reducing the effectiveness of the protective coating.

5.1. Optical behaviour of the UV protective coating

The coatings present very strong absorption in the 275–400 nm range while having a thickness of only 1 μm. The protective film reduces the intensity of the UV light reaching the substrate to less than 7% of the incident radiation, providing an efficient protection against the UV radiation. On the other hand, the coatings show a very high transparency in the visible range and high optical quality, allowing the application of the protective films without affecting the optical properties of the substrate. The absorption spectrum of the UV-protective coating is shown in Fig. 18.

In order to establish the efficiency of the UV-protective coatings, two different photodegradable materials were coated with the UV-protective coatings: the first consisting of a fluorescent dye-doped film and the second consisting of a tile painted with organic dyes. An optical setup (Fig. 19) was designed to monitor the optical properties of the protected materials during irradiation with intense

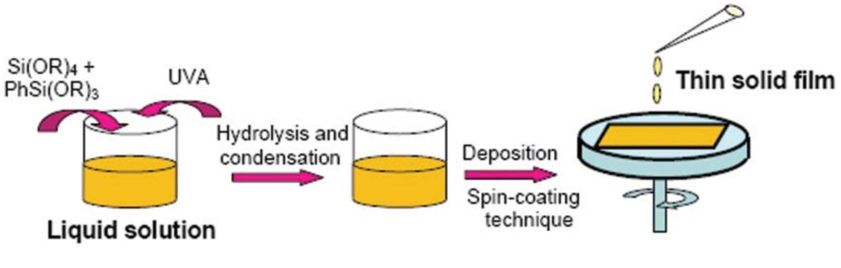

Fig. 17 Deposition of UV-protective coatings by the Sol–Gel process.

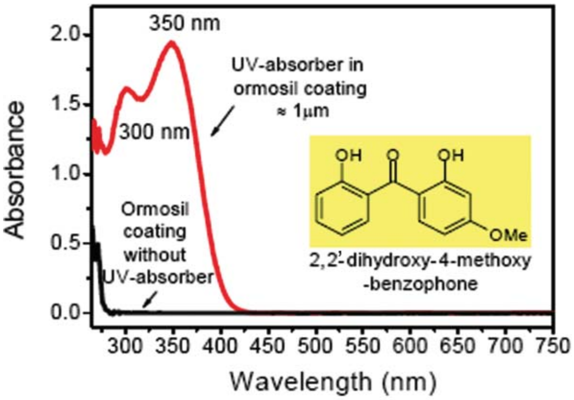

Fig. 18 Absorption spectrum of the UV protecting film (1 µm) with and without the UV-absorber molecule (34 wt%).

UV light in transmission and reflectance geometry for the transparent fluorescent film and the opaque painted tile, respectively.

5.2. Effect of the protective coating on the photodegradation of fluorescent-dye doped films

The advanced optical device consists of fluorescent dye molecules (rhodamine 101) dispersed in a transparent thin film. The dye molecules embedded in the film are rapidly degraded when exposed to UV light (0.4 mW cm^{-2} in the UV-B range). The fluorescent film was coated with a UV-protective coating, to increase the durability of the optical device. The deposition of the UV-protective films on top of the rhodamine thin films does not affect the optical properties of the dye, as it is fully transparent in the visible range. Moreover, the very strong absorption of the coating in the UV range drastically reduces the UV light reaching the fluorescent dye, which is responsible for its photodegradation. This effect can be observed in Fig. 20, where the spectra of the rhodamine thin film uncoated and coated with the UV protective coating are given.

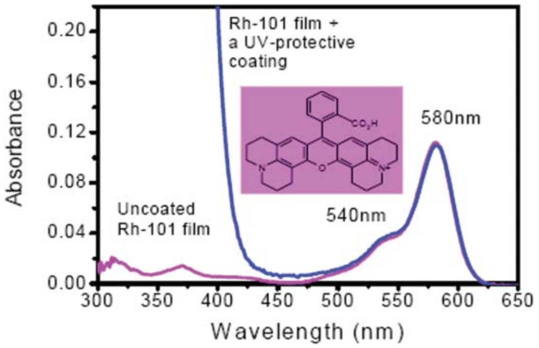

Fig. 20 Absorption spectra of the fluorescent film with or without the protective coating.

The degradation of the fluorescent film upon exposure to intense UV radiation was studied in coated and uncoated samples, monitoring the intensity of the absorption maximum of the dye as a function of the irradiation time at constant temperature. A noticeable reduction in the rate of degradation was observed for the coated samples as compared with the uncoated fluorescent samples. The photodegradation of 20% of the dye molecules is 14 times slower in coated samples, as shown in Fig. 21a. The photographs in Fig. 21b show the uncoated and coated samples after irradiation with UV light. A dark spot can be observed in the uncoated sample due to the degradation of the rhodamine dye by UV light. No such effect is visually apparent on the coated sample, giving direct evidence of the high efficiency of the UV protective coating.

A faster photodegradation of the fluorescent dye was observed as the temperature of the sample was increased. However, the protective coatings show very efficient performance even at 65 °C, which enables the UV-protective coatings to be used in outdoor applications.

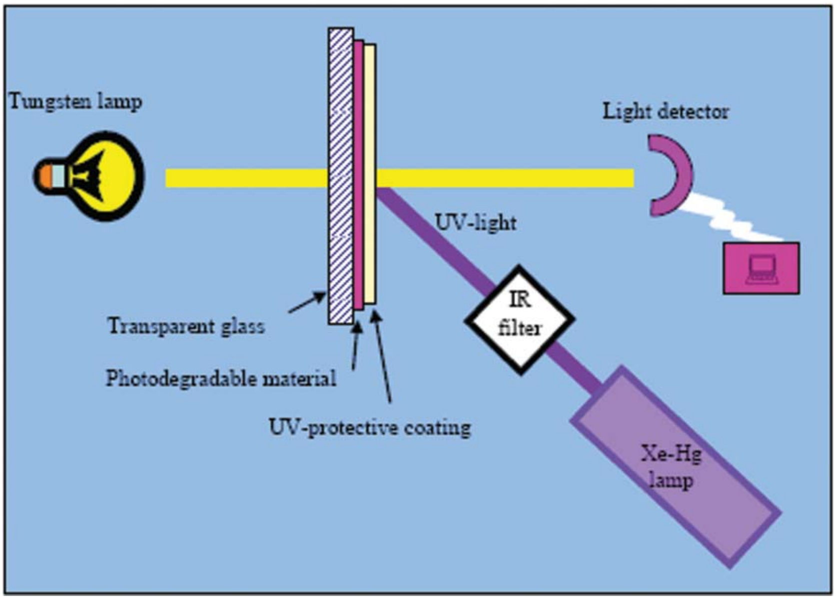

Fig. 19 Optical setup for photodegradation measurements.

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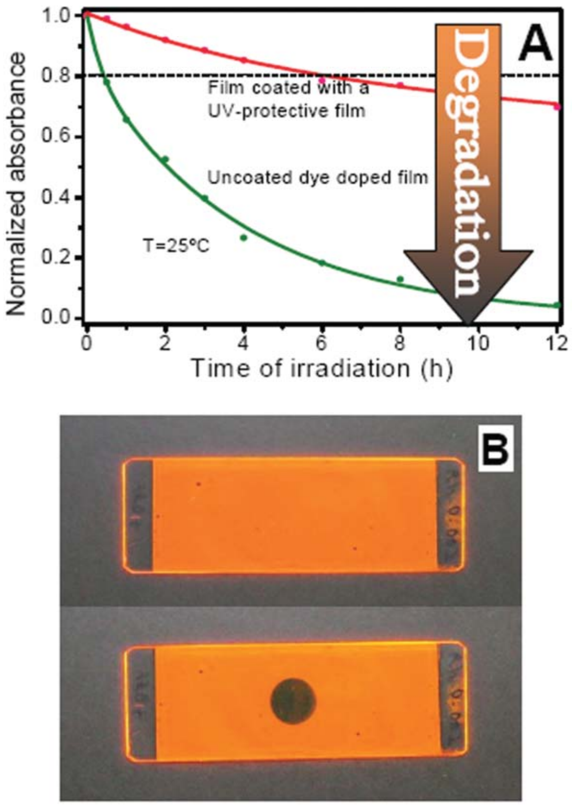

Fig. 21 Photodegradation of the fluorescent dye in samples coated and uncoated with the protective film: A) Absorbance of the fluorescent dye *vs* time of irradiation; B) Photographs of the samples after irradiation with UV light. The coated sample (top) remains unaffected, while the uncoated sample (bottom), shows a dark spot due to the damage by UV light.

5.3. Effect of the protective coating on the photodegradation of a tile painted with organic dyes

The opaque tile painted with organic dyes was irradiated with intense UV light (100 W Xe(Hg) lamp at a distance of 45 cm). The irradiation damages the dyes producing their discoloration (blue to yellow), as shown in Fig. 22. Fig. 23 shows the diffuse reflectance spectra of the coatings, where this colour change can be measured.

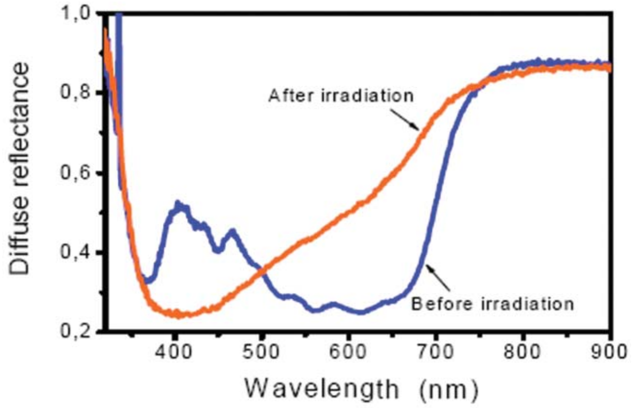

Fig. 23 Diffuse reflectance spectra of the painted tile before and after irradiation with intense UV light.

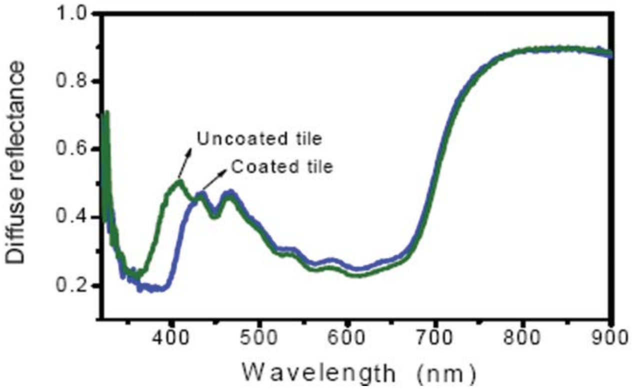

Fig. 24 Reflectance spectrum of the tile uncoated and coated with the UV-protective film. The similarity of the spectra in the visible range ensures that no changes are infringed to the visual aspect of the samples.

The UV-protective coatings have been applied to the tile to establish their effectiveness. The spin-coating technique was used for the deposition of the film on the painted tiles. The applied coating does not affect the colour properties of the paint (visible range), as can be observed in the reflectance spectrum of the uncoated and coated tile, shown in Fig. 24. The spectra show also the strong absorption of the UV-protective coating in the UV range, which is responsible for the protective capabilities of the coating.

The photodegradation of the tile paint upon prolonged irradiation with UV light was measured on samples coated and uncoated with the UV-protective films at constant temperature. A drastic increase of the durability of the paint on the tile

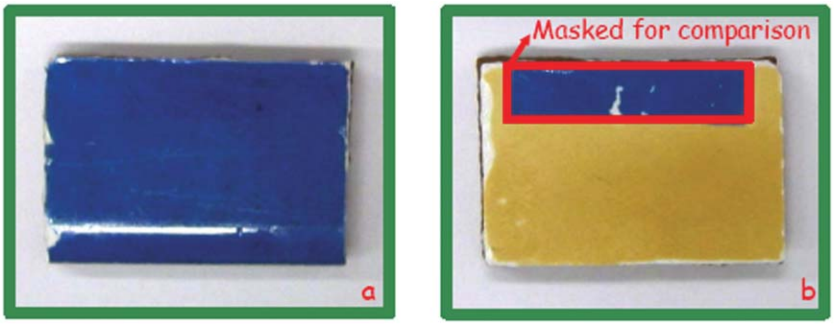

Fig. 22 The degradation of a painted tile by UV radiation: (a) before and (b) after irradiation with intense UV light.

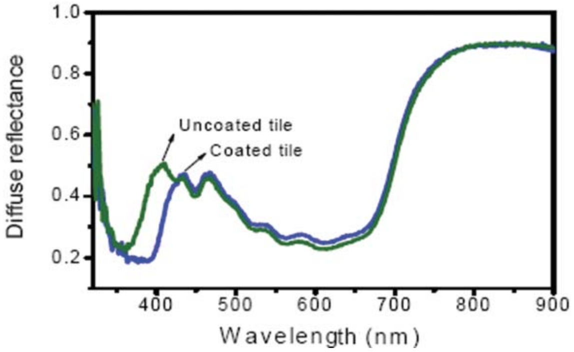

Fig. 25 Degradation of uncoated painted tile samples, shown in Fig. 22 and samples coated with the UV-protective coating. The degradation was monitored measuring the reflectance of the sample at 632 nm as a function of the irradiation time.

(more than 28 times) was observed by the application of the UV-protective coating (Fig. 25).

6. Conclusions

Much effort has been devoted to reduce or eliminate the damaging effects of solar and artificial UV radiation on materials in order to increase their durability. The extensive use of organic materials, such as polymers, paints, artwork pigments, dyes, and others, on common articles, makes efficient UV-protective coatings, that do not affect the functionality of the degradable material, a necessary and valuable tool.

We have recently developed a highly effective UV protective coating based on the dispersion of highly efficient UV-absorber molecule in a sol–gel hybrid organic–inorganic ormosil matrix. Using hybrid matrices allowed us to control the properties of the host matrix in order to optimize the environment where the UV-absorber molecules will be entrapped.

The ability to apply the protective coating on heat sensitive materials is a very important advantage, as most organic based articles or products that need to be protected can not undergo a heat treatment. On the other hand the fact that the coating is fully transparent in the visible range allows the usage of the coatings on optical devices or coloured substrates without altering their properties.

The protective coating was applied to two different degradable materials: a fluorescent advanced optical device and a tile painted with organic dyes. The first exhibited a rapid degradation upon exposure to UV light, while the tile showed a strong discoloration of the paint. The high efficiency of the coatings was evidenced by the drastic reduction of the degradation observed in both protected substrates when exposed to intense UV radiation. The durability of the degradable substrates was increased by a factor of 14 and 28 for the fluorescent and painted tile respectively.

The ability to increase the durability of outdoor products, that uncoated can withstand solar radiation for months or years, by a factor of 14 or more makes the protective coatings very attractive for use in commercial applications.

Therefore, the UV-protective coatings can be applied to a wide range of UV degradable substrates, from paints, plastics or optical devices in outdoor applications to artwork in museums, where paintings and sculptures should be specifically protected against the damaging flashlight of photographic cameras, without making any change to their visual aspect.

In this way, the very effective Sol–Gel ormosil protective coatings can be used to reduce UV light reaching the organic substrates, and to increase the lifetime of photosensitive materials from a scale of months to one of years, when exposed to outdoor solar radiation.

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