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To cite this version:

Davy-Louis Versace, Louise Breloy, Estelle Palierse, Thibaud Coradin. Contributions of photochemistry to bio-based antibacterial polymer materials. Journal of materials chemistry B, In press, 10.1039/D1TB01801A . hal-03450996

HAL Id: hal-03450996

https://hal.sorbonne-universite.fr/hal-03450996v1

Submitted on 26 Nov 2021

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Contributions of Photochemistry to Bio-based Antibacterial Polymer Materials

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Abstract: Surgical site infections constitute a major health concern that may be addressed by conferring antibacterial properties to surgical tools and medical devices *via* functional coatings. Bio-sourced polymers are particularly well-suited to prepare such coatings as they are usually safe and can exhibit intrinsic antibacterial properties or serve as hosts for bactericidal agents. The goal of this Review is to highlight the unique contribution of photochemistry as a green and mild methodology for the development of such bio-based antibacterial materials. Photo-generation and photo-activation of bactericidal materials are illustrated. Recent efforts and current challenges to optimize the sustainability of the process, improve the safety of the materials and extend these strategies to 3D biomaterials are also emphasized.

1. Introduction

Bacterial infection has been a constant plague along medicine history. Only in the mid-XIXth century was the need for antiseptic surgical procedures clearly expressed by Lister, based on the works of Pasteur. In particular the requirement for operating rooms with controlled atmosphere, asepsis of medical staff wearings and sterilization of surgical tools were identified. Based on these founder concepts of modern surgery, tremendous progresses were made but a study from the late 70's still reports post-operative wound infections rates of *ca*. 5 % in clean operation rooms, with large variability as a function of patients state[1]. Very importantly, this study pointed out that more than 40 % of the infecting bacteria were endogenous, *i.e*. present in the patient body at the time of the surgical procedure. Since then, guidelines have been proposed to tackle these now-called surgical site infections (SSI) but these numbers have remained stable in developed countries[2, 3]. However, the ongoing phenomenon of increasing antibacterial resistance, described by the World Health Organization as "one of the biggest threats to global health, food security, and development today", raises major concerns for the years to come.

One of the most commonly encountered bacterial strain in SSI is *Staphylococcus aureus*. It is present both outside (skin) and inside (mucous membranes of organs, especially in the nose) the human body, including 15 % of healthy patients[4]. Whereas contamination from the skin population during open surgery may be avoided by aseptic treatment of the wound area, addressing bacterial proliferation after wound surgical or physiological closure is much more challenging. This is usually tackled by systemic administration of antibiotics which, together with contributing to the overuse of such drugs, may impact other organs. Thus, conferring antibacterial properties to implanted devices would constitute a more local and specific therapeutic solution[5-7].

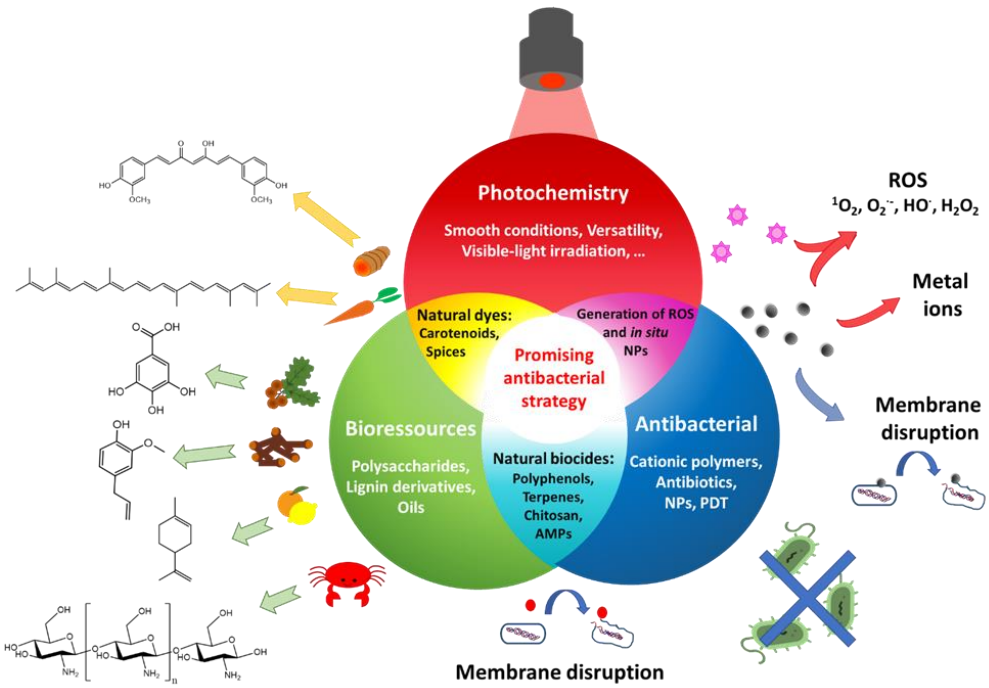
However, care must be taken that modification of the implants does not interfere with the bio-integration of the material or, even worse, is detrimental to the activity of other cells. In this perspective, the use of biocompatible, *i.e*. non-toxic and bioactive, natural molecules as key elements for the elaboration of such coatings appears particularly relevant. On this basis, bio-based polymers have already been widely used for medical applications, notably for tissue engineering or drug delivery[8-10]. These include natural polymers such as polysaccharides, bioengineered polymers and artificial polymers derived from bioresources. Thanks to their abundancy and their wide structural diversity, they constitute a rich platform of base material with versatile physicochemical properties and adapted to chemical modification[11].

Effective mechanisms of defence already exist in nature[12, 13]. For instance, the structuration of some animal skins or vegetal leaves at nanoscale is able to prevent bacterial adhesion, constituting

antifouling surfaces[14]. The production and release of natural biocidal molecules, such as antibiotics[15], essential oils[16], or antibacterial peptides[17], enable them to fight external attacks. Another mechanism of defence is the generation of Reactive Oxygen Species (ROS), called oxidative burst, when pathogenic species are detected[18]. All these mechanisms, demonstrated as effective in nature, can be mimicked by synthetic equivalents[13, 14, 19, 20]. However, to ensure cyto- and biocompatibility as well as biodegradability, natural compounds should constitute the most suitable source of molecules to design antibacterial coatings for medical applications[8-11].

Over the last few years, several reviews have highlighted the contribution of biomacromolecules to the design of antibacterial systems, either from a general perspective or focusing on specific polymers[21-28]. Many of these reviews[12, 13, 29-31] clearly demonstrated that, besides antibacterial efficiency, several other properties of the coatings such as mechanical strength or thermal stability, need to be optimized. However, among the various synthetic strategies that have been applied and/or developed in this field, the specific contribution of photochemistry has, to our point of view, so far been neglected in the literature reviews, despite its many advantages in terms of versatility, mild conditions and spatio-temporal control over the reaction.

The following review therefore aims at providing a timely picture of the application of photochemical processes to the synthesis of antibacterial materials using bio-sourced molecules and macromolecules (Scheme 1). We first review the photo-induced synthesis of antibacterial materials from molecular (essential oils and their components) and macromolecular (cationic polymers) bio-sources. The application of photochemistry to antibacterial bio-nanocomposites is also presented. In a second part, the integration of photosensitizers as photo-bactericidal agents in bio-based matrices is discussed, with a particular highlight on combined strategies where light is used for both material synthesis and as the source of antibacterial agents. Main challenges and research perspectives in this field are provided as concluding remarks.



Scheme 1. Judicious combination of photochemistry and bioresources toward development of promising antibacterial strategies

2. Photo-generation of Antibacterial Materials using Bio-resources

2.1 Why photochemistry?

In recent years, light-induced polymer chemistry has received a revitalized interest due to the development of new emerging photo-initiating systems and is now encountered in numerous applications or promising scientific areas[32-35].

The benefits of photochemistry are numerous[36] and concern (*i*) the rapid cure/reaction time (a few seconds or minutes), permitting high production rate ; (*ii*) the low energy requirements as experiments can be done at very low light intensities ; (*iii*) low temperature treatments (room temperature and below) suitable for heat-sensitive supports ; (*iv*) the absence of solvent, avoiding the release of volatile organic compounds; (*v*) application versatility, small space requirements, easy to use, easy maintenance, low investment ; (*vi*) low level of waste ; (*vii*) moderate costs of photo-initiating systems ; and (*viii*) spatiotemporal control.

All these aspects justify the fast growth of photochemistry as green process in the context of sustainable development. However, it was reproached to photochemistry to occur mostly under harmful UV radiations, and to be often based on toxic petro-sourced components. To face these issues, research of the last decades has shifted towards several directions, notably to reduce energy consumption and environmental impact.

Among these, the use of new light sources is of particular interest. For instance, light-emitting diodes (LEDs) exhibit many advantages over classical UV lamp sources (mercury arc lamps, doped lamps or excimer lamps) such as low heat generation, low energy consumption, less maintenance, operating costs and less space requirements[37]. Laser sources are also of high interest as they offer a high energy concentration in a small and focused volume that allows the instantaneous polymerization overcoming issues of oxygen inhibition but also reduce side reactions[38]. The possible use of household lamps, *i.e*. standard and commercial devices, is also highly looked for, as they use lower electrical power and can present a low divergence of light beam.[39] Ultimately, formulations that can be cured by sunlight have been reported[39]. In parallel, identification or development of visible-light photo-initiating systems is required[40-42].

In terms of environmental impact, photosensitizers with high quantum yields should permit the use of low concentrations, limiting the risk associated to chemical toxicity. Development of new water-based photoinitiating systems or formulations to avoid organic diluting media and release of volatile organic compounds (VOCs) is also under study[43]. Meanwhile, an intense research is devoted to the design of novel photopolymerizable monomers or green photoinitiators from bio-sourced molecules which can be easily functionalized with (meth)acrylates, epoxy or vinyl moieties[44-47].

The renewal of photochemistry based on lower energy light sources and more biocompatible compounds opens huge opportunities for biomedical applications[48-52], including for antibacterial applications as detailed below.

2.2. Materials based on natural antibacterial molecules from plants.

To face the development of antibacterial resistance, the use of natural active products has attracted much attention in the last decades[53]. Secondary metabolites extracted from plants, such as polyphenols or terpenes, are of particular interest as they are often involved in their defense mechanisms against predation by microorganisms, insects and herbivores[54]. Many of the most volatile ones are concentrated within so-called essential oils[16] (EOs), are traditionally obtained by steam distillation, and used for household (insect repellent) and antibacterial purposes. Besides, Faleiro and Swamy et al. have recently demonstrated that the antimicrobial efficiency of the EOs[55, 56] is governed by the proportion of various chemical groups (aldehydes, phenols, terpenes) in the formulation and by their structural configurations. However, it is well-established now that the presence of EOs can cause potassium ion leakage, degrading thus the membrane integrity of the bacteria[57]. The resulting permeability of the membrane affects various vital processes, notably those ensuring energy

conversion, nutrient assimilation, or growth regulation. Several possible sites of damage have been identified[58], such as cell wall, membrane proteins, and cytoplasmic membrane.

As a mixture of components, EOs also have a complex physico-chemical behavior and cannot be used as such to prepare a stable coating but can be used as additives to polymer matrices[59, 60]. Therefore, many components isolated from EOs have been used both as biobased monomer to form a polymer-based material and as antibacterial agent[45, 61] Some of them, such as Eugenol, Linalool or Limonene, have intrinsic photo-reactive functions, such as allyl which can undergo thiol-ene reactions[62] (**Figure 1**). Otherwise, they are easily modified to turn them into photoactive monomers: allyl groups can be epoxidized[63, 64], and phenols, such as Thymol and Carvacrol, can be functionalized with allyl, epoxy or acrylate groups.

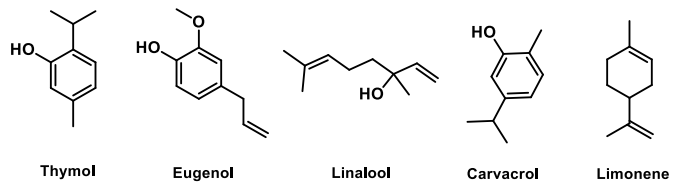


Figure 1. Essential oil extracts used in antibacterial coatings

In particular, Eugenol, extracted from clove, whose mechanism of action against bacteria is well-known[65], has been used to design photopolymerized networks[66, 67], that can exhibit antibacterial activity[63, 68-70]. Either eugenol or epoxy-eugenol were used as monomers for combining thiol-ene and cationic photopolymerization process. In the first case, enhancement of antibacterial activity was achieved by encapsulation of carvacrol or tannic acid[68]. As the two additives were not chemically conjugated to the network, they were able to migrate outside of the polymer network but with different kinetics due to their differing sizes and interactions with the matrix. As a consequence, carvacrol-incorporating networks exhibited high antibacterial activity against both *E. coli* and *S. aureus* on the short term while those embedding tannic acid preserved 100 % of their initial antioxidant activity after 2 months. In the second case, epoxy-eugenol was used in UV-induced cationic polymerization alongside resorcinol diglycidyl ether[63]. The presence of epoxy-eugenol not only allowed to tune the mechanical and thermal properties of the resulting polymer films but also confer them antioxidant and antibacterial activity, as the radical scavenging activity of the materials increased from 5 to 75 % with the introduction of 10 wt.% of epoxy-eugenol. Recently, unmodified eugenol was also incorporated as allyl monomer and antibacterial agent in a photogenerated limonene-based network[69]. Two epoxy derivatives of limonene, limonene-1,2-epoxide and dipentene dioxide, were copolymerized with eugenol by cationic and thiol-ene photopolymerization. To perform a cure under visible light, a natural dye, beta-carotene, was used as a photosensitizer. The introduction of 25 wt%

of natural eugenol in the limonene-based formulation permitted to record a high antibacterial effect against *E. coli* and *S. aureus*.

Interestingly, Liu et al. directly turned an antibacterial polyphenol, tannic acid, into a UV-photopolymerizable monomer by partial grafting of methacrylate functions[71]. By varying the degree of methacrylate functionalization, a series of materials with various properties were obtained. Indeed, as the antibacterial effect is mainly due to the phenol group, increasing grafting had a detrimental impact on antibacterial properties while enhancing stability and mechanical properties.

In order to valorize terpenes and to move towards alternative raw materials, Langlois and co-workers suggested the utilization of sustainable polymers[72], poly(hydroxyalkanoate)s (PHAs) *e.g.* aliphatic polyesters produced by bioconversion as intracellular nutriment storage materials inside bacteria, and linalool (a monoterpene extracted from lavender oil) to develop co-networks by photo-induced thiol-ene reactions. These bio-based materials not only demonstrate higher elasticity properties in comparison with those of native PHAs but also antibacterial properties against *E. coli* and *S. aureus* decreasing by 63% and 82% their adhesion respectively. The combination of essential oils and bio-based monomers could offer a wide range of possibilities for the synthesis of innovative antibacterial materials under light irradiation[72].

2.3. Materials Incorporating Positively Charged Molecules/Polymers.

The use of cationic derived molecules (peptides) or natural polymers (starch, chitosan and derivatives, polyhydroxyalkanoates) which properties can be easily tuned by simple (photo)chemical modifications are perfectly adapted to the synthesis of new positively charged antibacterial materials. The most commonly accepted mechanism for the antibacterial properties of cationic polymers[73-76] combines their positive charge, which make them likely to interact with the negatively charged cell wall (due to teichoic acids in Gram-positive cells and phospholipidic outer membrane in Gram-negative ones), and their amphiphilic character, inducing a membrane disruption. Although the mechanism is complex, it can be summed up in four main steps: (1) Rapid adsorption via cationic groups on the negatively-charged bacterial cell surface, (2) diffusion of the hydrophobic backbone through the cell wall and alteration of its permeability, (3) interaction with phospholipids of the cytoplasmic membrane, disruption though micelle-like structures formation, increase of permeability (K^+ loss) and electrolyte balance disorder and (4) loss of membrane function, inducing precipitation of intracellular constituents and cytolysis. In addition, many inner cell compounds contain sulfonates or phosphates groups, likely to interact with cationic groups. It can trigger several “untargeted” events, which can take place simultaneously or successively[77]. Some divergences of efficiency have

been observed for Gram-positive and Gram-negative bacteria. Because of the higher protection offered by the outer membrane, it seems that Gram-negative bacteria are less sensitive to cationic polymers. Besides, another biocidal mechanism has been highlighted for chitosan concerning Gram-negative bacteria where the polymer chain is hypothesized to block the transport of essential nutrients, inducing an internal osmotic pressure and leading to the cell death[26, 78].

After these antibacterial mechanism discussions, we can first focus on the antibacterial peptides (AMPs) whose production in Nature is intended to eliminate bacteria. They are produced by a wide range of living organisms and have applications for the cure of many infections[79-81]. Despite their wide use in several fields, such as biomedical, food conservation, or soil decontamination, these low molecular weight antibacterial agents are currently criticized for their residual toxicity. Additionally, their rate of diffusion is hard to control, which means that they afford a protection on a relatively short period of time. Therefore, the possibility to graft them to higher-molecular-weight structures, or to combine them by polymers, has been investigated to achieve higher stability and longer lifetime. Indeed, association of AMPs with polymers hydrogels has been reported on several occasions[82]. For instance, biomaterials incorporating the Tet213 AMP were prepared from gelatin methacryloyl by free-radical photopolymerization under visible light using the commercial FDA-approved photo-initiating system, eosin Y/triethanolamine/*N*-vinyl caprolactam[83, 84]. However, because the peptide is not chemically bond to the hydrogel network, it is mostly released within a few hours. In contrast, investigations concerning antibacterial materials functionalized with AMPs *via* photochemical processes are scarce. A major concern is that some AMPs tend to lose their efficiency when immobilized in a non-specific manner on a surface[85]. However, the thiol group of cysteine (Cys) opens great opportunities of grafting by thiol-ene process. For example, the photo-grafting of Cys-HHC10 AMP by thiol-ene click chemistry on a biobased polymer hydrogel was reported[86]. This hydrogel was prepared by combining of furyl-modified sodium alginate and bismaleimide-PEG through Diels-Alder "click chemistry", ensuring good mechanical strength. The AMP-functionalized hydrogel, prepared under UV light irradiation, in presence of Irgacure 2959, showed a good cytocompatibility to Human Skin Fibroblasts (HSF) cells and high antibacterial activity against *E. coli*. An all-photochemical process was also to design antibacterial macroporous sponges for haemorrhage control. Starch was modified with norbornene anhydride, and a hydrogel was formed under UV by thiol-norbornene reaction with PEG-thiol, in the presence of Irgacure 2959[87] (**Figure 2**). In a second step, the same process was used to graft Cys-KR12 AMP on the surface of the material. In addition to the haemostatic activity of the sponges, efficient antibacterial activity was recorded against *S. aureus*, *Staphylococcus epidermidis*, *E. coli* and *MRSA*.

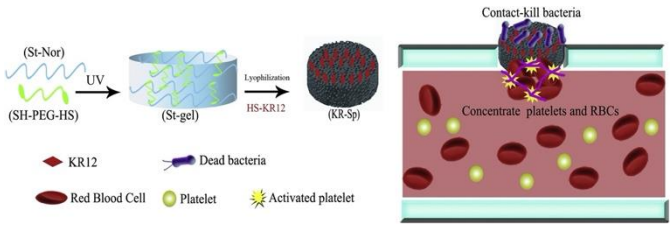


Figure 2. Starch-based hydrogels polymerized under UV irradiation and modified with the KR12 peptide combine antibacterial activity with haemostatic properties[87]. Reprinted with permission from reference 87. Copyright (2019) Elsevier.

As an alternative to peptides, biomimetic polymers[88] have been considered. In particular, cationic homopolypeptides, such as poly-L-lysine, or copolypeptides have also been considered. Usually, the photoactive moiety is a methacrylamide function introduced by reaction of polypeptide amine groups with methacrylic acid *via* [1-ethyl-3-(dimethylamino)propyl]carbo-diimide hydrochloride (EDC) coupling with NHS[89]. Combination of polypeptides with complimentary properties was also reported[90]. In this work, antibacterial poly(L-lysine-co-L-phenylalanine) and antifouling polysarcosine were synthesized and functionalized with a methacrylate group. The two macromonomers were copolymerized under UV on a polydopamine surface. While being cytocompatible towards mouse fibroblasts, the resulting surface demonstrated a dual functionality: antifouling, by limiting adhesion of platelets and proteins, and contact-killing activity against *E. coli*, *P. aeruginosa* and *S. aureus*. In another work, ε-polylysine-glycidyl methacrylate (ε-PL-GMA) was copolymerized to γ-poly(glutamic acid)-glycidyl methacrylate (γ-PGA-GMA) under visible light using Lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP) as a photoinitiator. The resulting biocompatible hydrogel has demonstrated strong antibacterial activity against *S. aureus* and *E. Coli*. Thanks to its injectability and wound healing properties, this formulation may be promising in the treatment of skin infections[91].

Besides peptide-based structures, several polysaccharides have intrinsic antibacterial properties or can be modified to bear the suitable cationic moieties. The most popular one is chitosan[26] which remains a reference in the field of cationic polymer, as it has the advantage to be bio-sourced, biocompatible, biodegradable and nontoxic. Contrary to most other polysaccharides, chitosan has amine functions on its backbone, which makes it easily modified on multiple points. For instance, and for the photogeneration of chitosan derived antibacterial materials, a widely used method is the grafting of methacrylate groups on chitosan using methacrylic acid and EDC/NHS coupling[89, 92]. Photo-induced copolymerization with other functional (bio)-polymers was also described[93, 94]. For example, methacrylate-functionalized chitosan was copolymerized with PEG-diacrylate by free-

radical polymerization. A total conversion of acrylate groups was reached under UV irradiation within 100s, using Type I photoinitiator *i.e.* hydroxy-cyclohexyl-phenyl-ketone. A total inhibition of *E. coli* and *S. aureus* was observed, and the contact-killing action of chitosan-PEG surfaces was evaluated *via* a comparison to an antifouling PEG material after 6 months[94]. A second example highlighted the combination of a methacrylate-functionalized chitosan and a thiol-functionalized ε-poly-L-lysine *via* thiol-ene reaction under UV for 12h using DMPA as photoinitiator[93]. The obtained cationic peptidopolysaccharide has shown antibacterial activity against *E. coli* and *P. aeruginosa* as well as *Enterococcus faecalis* and MRSA.

Carbohydrates devoid of amine functions can also be modified to bear antibacterial moieties. Active functions can be introduced by modification of the OH groups. In the case of starch[95], a one-pot synthesis with a mixture of epichlorhydrin and *N*,*N*-dimethylallylamine permitted to add allyl groups on polysaccharide chain while forming quaternary ammonium groups. To this end, photo-induced thiol–ene reactions were used to synthesize hydrogels from the allyl-functionalized cationic starch-derivatives and a water-soluble photoinitiator (2-hydroxy-4′- (2-hydroxyethoxy)-2-methylpropiophenone) under UV irradiation (Figure 3). These hydrogel samples demonstrated antibacterial properties by successfully inhibiting the growth of three bacteria strains *i.e. E. coli*, *S. aureus* and *P. aeruginosa* (killing efficiency > 99.9%), hence confirming their potential uses as antimicrobial materials for preventing infections.

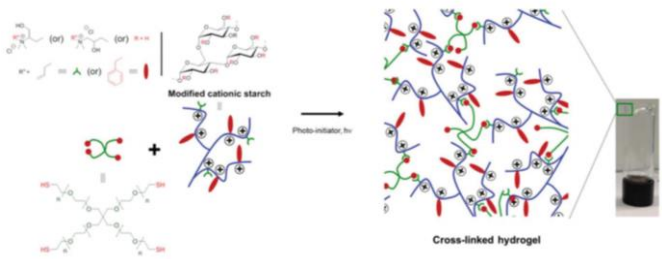


Figure 3. Photo-induced synthesis of starch-derived hydrogels by thiol-ene process under UV irradiation[95]. Reprinted with permission from reference 95. Copyright (2019) Royal Society of Chemistry.

Another strategy relies on the use of UV-active reagents that can attach to C-H bonds. For example, conjugates of dodecyl-alkylated quaternary ammonium or polyethyleneimine with benzophenone side chain could be grafted under UV irradiation onto cotton fabrics[96]. Cross-linked coatings firmly adhering to the fabrics were obtained, exhibiting tremendous antimicrobial activity against *E. coli* and *S. aureus* (> 99% of inhibition). Alternatively, a polyamine coating can be first formed on the targeted surface *via* UV-photopolymerization through peroxide decomposition, followed by a quaternization of the cellulosic photo-grafted surface. This surface functionalization technique

allowed to confer antibacterial properties against *E. coli* killed by contact and depend on surface ammonium concentration[97].

Photochemistry also allows to achieve grafting from reactions *via* hydrogen abstraction. Such a possibility was more particularly explored to confer antibacterial properties to Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV). For instance, polymerization process was initiated under UV irradiation *via* abstraction of hydrogen on PHBHV surface by water-soluble ketone photoinitiating systems[98] (**Figure 4**). This simple photoinduced method allowed the grafting and the radical photopolymerization of cationic monomers to PHBHV surface, leading thus to the synthesis of new antibacterial surfaces. The surface could also be activated by aminolysis reaction, followed by the grafting of a thiocarbamate derivative, used as UV-photo-initiator[99] to tailor the surface properties of PHBHV surface. The antibacterial effect of the resulting surfaces was higher than 90% inhibition for both *E. coli* and *S. aureus*. Even if cationic based natural materials seem to be a serious alternative to petro-sourced polymers, the incorporation of metal nanoparticles inside photoinduced materials also appear as an efficient strategy to fight adhesion and proliferation of bacteria.

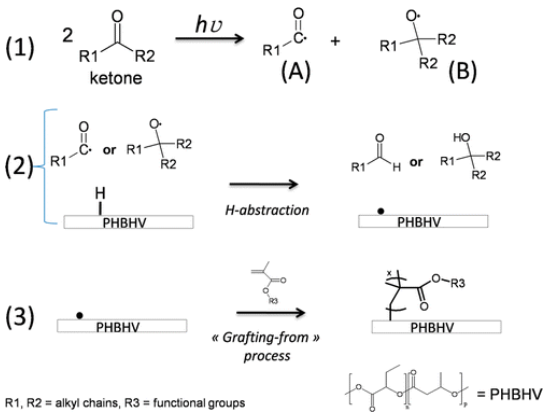


Figure 4. Photochemical modification of Poly(3-hydroxybutyrateco-3-hydroxyvalerate) (PHBHV). Under UV irradiation, photoinitiating ketones (1) induce H-abstraction of the PHBHV surface (2) allowing polymerization of methacrylate derivatives *via* a grafting from process. Reprinted with permission from reference 98. Copyright (2014) American Chemical Society.

2.4. Materials Incorporating Nanoparticles.

The design of antibacterial materials by incorporation of nanoparticles inside a polymer matrix has become very popular[100-102]. Indeed, the antibacterial properties of many inorganic nanoparticles (NPs), such as silver[103], copper[104], TiO_2[105], and ZnO[106], have been long known and used[107, 108]. Several mechanisms are responsible for the antibacterial properties of metal NPs: cell membrane

damage, interference of metal ions with intracellular chemical processes, and production of radical oxygen species (ROS).

i) The main pathways for the antibacterial effect of NPs consists in producing ROS, including O_2^-, HO_2 and HO radicals[109]. They can be produced by photo-activation (photo-generated holes and electrons) or simply by reducing oxygen molecules. ROS are able to degrade the outer membrane, and once inside the cell, can interfere with several processes. Although ROS are naturally produced in the cell, their amount is regulated. Their over-production can lead to oxidative stress, which damages the components of the bacteria.

ii) NPs can also release bactericidal metal ions. These ions, such as Ag^+, easily penetrate in the bacteria cytoplasm. They are likely to interact with thiol and phosphorus groups, which are largely present in the cell. Thus, numerous proteins containing cysteine may be disactivated in contact with silver ions[110]. It has also been observed that in presence of silver ions, bacteria DNA becomes condensed to protect itself from this external attack. Silver ions also interact with amide links of peptide bonds, and with oxygen of carbonyl bonds. They can also inactivate vital enzymes, such as those of respiratory chain, and therefore disrupt normal physiological processes, leading to cell death[108, 109, 111].

iii) It has also been shown that NPs can damage the cell through other non-oxidative physiochemical processes, providing an explanation of their strong antibacterial activity in the dark. Their specific size range make them prone to interact with bacteria cell wall and alter the membrane permeability[109, 112].

These three quoted mechanisms are still discussed and under investigation[108, 113]. Moreover, it has been highlighted that they can occur simultaneously[109]. Therefore, although a resistance to silver ions has emerged among some bacterial strains[114], it should be difficult for bacteria to establish a defence against metal NPs[108, 115, 116]. It explains the current great interest in exploring the use of nanoparticles as antibacterial agents in polymer materials.

Particularly, photochemical processes are very interesting not only for driving the polymerisation and the formation of the polymer matrix, but also for the *in-situ* synthesis of NPs under light activation.

To optimize antibacterial properties of such nanocomposites, it is necessary to tune the size and shape of NPs while controlling their repartition within the material. A first option is to disperse preformed nanoparticles into a monomer solution, which is then polymerized by light activation, so that the final material homogeneously encapsulates the NPs[117-119]. A typical example in the area of antibacterial biomaterials is provided by the work of Sani et al. that reported the thiol-ene photo-

crosslinking of methacrylated hyaluronic acid and thiolated elastin-like-polypeptide (ELP), in the presence of ZnO nanoparticles, leading to coatings exhibiting good bactericidal properties against MRSA[117]. Here hyaluronic acid and ELP were selected to achieve high mechanical stability and hydration level required for tissue engineering applications and the antibacterial properties were brought by the inorganic nanoparticles. Easy to implement, this strategy is applicable to almost all type of metal or metal oxide nanoparticles and photopolymerizable matrix[118, 120, 121].

An alternative approach is to use photochemical process to obtain the polymer matrix, which is then impregnated with metallic ions before inducing their reduction[122-124]. The above-mentioned dual chitosan/PEGDA system was used for this purpose[124]. In this study, cross-linked polymer networks shaped as cryogels have been used as a matrix to form size-controlled Ag NPs. Only short term and low antibacterial activity against *E. coli* was found in the absence of nanoparticles whereas the composites could demonstrate prolonged high inhibition ratio, thanks to the release of silver species from the matrix.

Finally, a one-step process can also be implemented, by taking advantage of the light irradiation of photopolymerization to simultaneously form *in situ* the NPs by photoreduction of a metal salt[125-130]. In this method, the concomitant formation of a polymer network around the particles enables a certain size and shape control. For instance, *in situ* synthesis of silver nanoparticles was achieved using a copolymer of sunflower oil and glycerol, which have undergone transesterification and methacrylation steps. Using a styrene co-monomer, polymerization was UV-induced using DMPA as PI, leading to materials efficient against *S. aureus*, *B. subtilis* and *P. aeruginosa*[125]. In another example, allyl-functionalized isosorbide was copolymerized by "click chemistry" with a thiol cross-linker derivative to form antibacterial coatings under UV light irradiation in the presence of DMPA[128]. Ag NPs were *in situ* generated and the photoinduced coatings demonstrated tremendous antibacterial properties against *E. coli* and *S. aureus* (**Figure 5**).

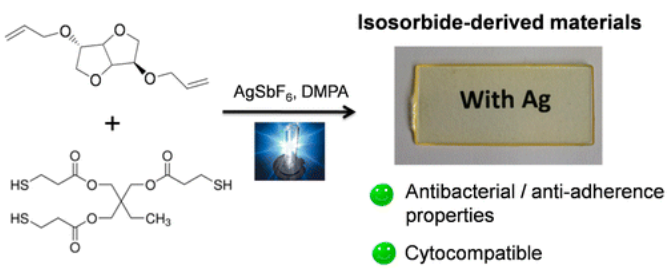


Figure 5. UV irradiation of allyl-functionalized isosorbide combined with trithiol and a silver(I) salt leads to transparent nanocomposites with antibacterial properties[128]. Reprinted with permission from reference 128. Copyright (2015) American Chemical Society.

2.5 Overview.

Overall, photochemistry seems well adapted to process bio-sourced molecules or macromolecules which would have been degraded by thermal treatments or difficult to modify chemically by other methods. Resulting materials often show high antibacterial activity and low toxicity. It is currently estimated that plant extracts, peptides, natural polymers or even metallic nanoparticles present a low risk of inducing serious drug resistance, although this may have to be reconsidered if their application becomes widespread. It is therefore important to explore other alternative mechanisms to induce bacterial death. An alternative promising way to use light to design antibacterial materials is photodynamic therapy. Inspired from the natural oxidative stress mechanism, it consists in the generation of ROS by organic compounds under irradiation. This mechanism can be integrated in bio-based polymers, in order to create photo-activated antibacterial materials. To go further, and as a perspective to develop, it is also possible to use photo-sensitive compounds both as photo-initiators for polymerization of a bio-sourced matrix, and as photosensitizers for biocidal activity.

3. Photo-active Antibacterial Materials from Bioresources

3.1. Photo-Generation of ROS.

Photodynamic therapy is mainly known for cancer treatment and has been recently extended to antibacterial therapy[131-134] (aPDT). It is based on the combination of light, a photosensitizer (PS) and oxygen. This combination permits to produce ROS responsible of cellular photodamage. Two different reactions can be observed: Type I process, where PS abstracts electron or hydrogen leading to redox reactions which allows the production of ROS and type II pathway, relying on an energy transfer reaction to molecular oxygen ($^3O_2$) thus leading to singlet oxygen[135, 136] ($^1O_2$). Singlet oxygen can oxidize biomolecules such as proteins[137], DNA[138] and lipids[139] but is limited by a short lifetime (~ 10^{-6}) and low diffusion distance[140] (< 250 nm). The main advantage of this approach is the lack of efficient innate defense in the bacteria, thus limiting the possibility to develop resistance[141].

Since the first description of photo-sensitization antitumoral activity[142] by Bellin et al. a wide variety of dyes an then, UV sensitizers have been studied in solution or integrated to polymer networks[143-145]. While grafting or encapsulation strategies similar to those previously described can be undertaken for such integration, additional constraints have to be considered, such as the transparency of the host material, its sensitivity to ROS and the short lifetimes of ROS, the later justifying the development of very thin films[146].

Some representative examples of antibacterial systems developed by combining PS with bio-sourced supports are gathered in **Table 1** and will be discussed afterwards.

3.1.1. Benzophenone and anthraquinone.

Benzophenone (BP) is an aromatic ketone having applications in many fields, notably for photo-chemistry[147]. It mainly absorbs UV light and is often more specifically used under UVA (365 nm) to form ROS including hydroxyl radical ($^{\bullet}OH$), superoxide ($^{\bullet}O_2$-), and hydrogen peroxide[148] (H_2O_2). Several studies have described the grafting of BP derivatives on cotton fabrics to create antibacterial textiles, using the pad-dry-cure method[149-153]. For instance, three derivatives of benzophenone 4-hydroxybenzophenone, 4,4-dihydroxybenzophenone, 4-chloro-4-hydroxybenzophenone were grafted using 1,2,3,4, butane *tetra*-carboxylic acid (BTCA) as a crosslinker, and sodium hypophosphite as a catalyst in a one-pot reaction. Despite providing better mechanical strength to the textile, the latter compound led to a lower antibacterial activity under light compared to hydroxy-benzophenone derivatives, which could be explained by its lower grafting rate and larger hydrophobicity[149] (**Table 1**). Another strategy of grafting has been investigated using a benzophenone derivative as cross-linker[152]. 3,3,4,4-benzophenonetetracarboxylic dianhydride (BPTCD) was grafted by esterification on cotton fibers through a similar pad-dry-cure method in presence of a catalyst at high temperature. The obtained cross-linked material shows wrinkle resistant properties, while preserving its mechanical strength. Bacterial inhibition under light reaches up to 99,99% d. Park et al. also used BPTCD but explored the possibility to use a choline chloride (ChCl)-based deep eutectic solvent, which has a lower environmental impact than classical organic solvents. The presence of ChCl quaternary ammonium in the samples gives them high antibacterial properties even without light irradiation[153].

Anthraquinone (AQ) derivatives have a structure close to benzophenone, and consequently a similar reactivity to light irradiation. They were also mainly incorporated in textiles to create antibacterial fabrics from bio-sourced or synthetic fibers[154-158] using traditional dyeing method. AQ acid dyes were directly applied on nylon, wool and silk using an acid dyeing process, and observed a large photo-bactericidal activity of the materials[156]. For instance, the Vat dyeing process was used to incorporate 2-ethylanthraquinone and Vat Yellow GCN in cotton fabrics (**Figure 6**). long-term antibacterial activity under UVA, keeping *E. coli* inhibition to 99.99% even after 10 washes of the sample, while the inhibition against *S. aureus* decrease from 99.99% to 60%[154] (**Table 1**). Later on, the double action of 2-ethylanthraquinone both as an antibacterial agent and as initiator for surface photopolymerization of methacrylate was used, after immobilizing the photosensitizer through Vat process on cellulose[157]. Under UVA, anthraquinone in its triplet state can abstract a hydrogen from

cellulose, the formed radical being able to initiate photopolymerization process. These fabrics could also inhibit both gram positive and negative bacteria at 99.99%.

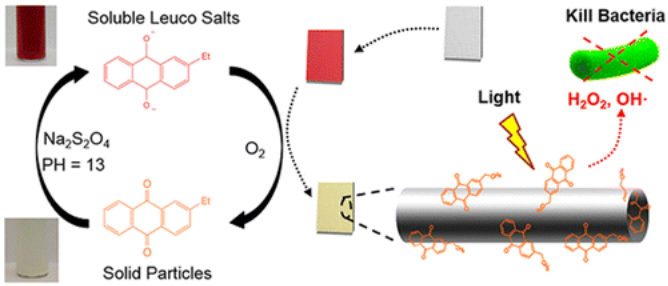


Figure 6. Photoactive coatings based on anthraquinone: ethylanthraquinone is grafted on cotton fabrics using the Vat process: the insoluble dye is turned soluble by sodium dithionite and used to impregnate the fibers before being reprecipitated by oxidation. Generation of ROS under UV light irradiation confers high antibacterial activity to the modified fibers. Reprinted with permission from reference 157. Copyright (2013) American Chemical Society

3.1.2. Phenothiazine and xanthene dyes.

Phenothiazine dyes are characterized by a heterocyclic aromatic structure and an absorption band between 600 and 800 nm[159]. The most common phenothiazines structures are methylene blue (MB) and toluidine blue O (TBO), but several other derivatives have also been widely studied such as dimethylene blue, azure A and azure B[160-162] in non-bio-sourced matrices[163], where their action has often been coupled with those of metal gold or silver nanoparticles[164-167]. Only Wilson et al. reported the incorporation of TBO without grafting in a simple biopolymeric matrix, cellulose acetate[168]. This material showed a great photo-bactericidal activity against *MRSA* and *P. aeruginosa*, 94% and 99.9% of cell inhibition after 24 h of visible light exposure, respectively. No leaching of MB has been observed, indicating that antibacterial activity originates from photo-generated ROS. In contrast, when MB was incorporated in PHB-PEG nanofibers, it has been suggested that the antibacterial effect was due to the dye release, as light transmittance through the polymer network was extremely low[169].

Xanthene derivatives constitute a well-known family of dyes, including Fluorescein, Eosin Y (EY), Phloxine B and Rose Bengal (RB). The latter is probably the most studied for antibacterial systems[170-175], for various applications requiring singlet oxygen production. EY was also incorporated in coatings[176] or fabrics[177]. Phloxine B has been used as antibacterial agent in polymer films activated by light[178]. It was incorporated in a cellulose material associated with polyvinyl amine via a Layer-by-Layer process, taking advantage of the negative charge of Phloxine B[179]. Its white light-activated antibacterial activity has been demonstrated against *P. aeruginosa* (Gram-), *Listeria monocytogenes* and *Bacillus anthracis* (Gram+). However, *Salmonella typhimurium* (Gram-) and *E. coli* (Gram-)

were only partially sensitive to the PS agent, probably due to the net negative charge on their surface (**Table 1**).

Some works have demonstrated the advantage of coupling xanthene dyes in singlet-oxygen-producing films, such as EY and RB[180], RB and phloxine B[181], or RB and fluorescein[182]. Moreover, the association of dyes from different families has also been demonstrated as an efficient option, such as RB and MB[183, 184], RB and BP[185], or MB and crystal violet[186-188]. For example, Decraene *et al*. produced cellulose acetate coating trapping both RB and TBO using a solvent evaporation method[189]. Targeting an application for health facilities, the lamp used in the experiment shows a spectrum similar to fluorescent luminaires in hospitals, and the tested bacteria were infused in human saliva. Photo-bactericidal action of this coating has been tested against *S. aureus*, a methicillin-resistant strain of *S. aureus*, *E. coli*, *C. albicans*, *Clostridium difficile*, and bacteriophage X174 (used as a model virus). Complete killing was obtained after 16 h for *S. aureus* and *E. coli* (**Table 1**). Following the success of this experiment, coatings have been evaluated in a clinical environment. However, no complete killing has been observed, which is understandable considering the uncontrolled environmental parameters compared to laboratory conditions[190].

3.1.3. Porphyrins and phthalocyanines.

The absorption spectra of porphyrin derivatives are generally characterized by an intense absorption band between 400 and 410 nm (Soret band) and weaker one (Q bands) between 530 and 700 nm depending on the substituents[191]. The potential of porphyrins for medical applications has been particularly highlighted, because some porphyrin derivatives are naturally present among crucial compounds of living organisms, such as haemoglobin, chlorophyll or vitamin B12. Perspectives concerning porphyrin compounds used as antibacterial agents has been recently reviewed[192]. The main photo-bactericidal pathway of porphyrin structures is assumed to be a Type II mechanism, leading to the formation of singlet oxygen[193]. It is probably involved in secondary reactions inducing the formation of oxygen radical species[194], such as $O_2^{\bullet-}$ or H_2O_2.

Interest of porphyrin compounds has been widely emphasized to create antibacterial textiles and, especially on cellulose support[195]. Ringot et al presented the first example of cotton fabrics with porphyrins as photo-bactericidal agents. A “click chemistry” reaction was used to bind acetylenic porphyrin derivatives to azide-functionalized cellulose in the presence of copper. This fabric showed an effective photo-killing of *E. coli* and *S. aureus*[196]. The influence of the charge of porphyrin structure has been evaluated by grafting anionic, neutral and cationic amino porphyrins on cotton. 1,3,5-triazine link has been used as a covalent bond between PS ang cellulose hydroxyl group, without

previous functionalization of the polymer surface. Under light irradiation, these fabrics efficient killed *S. aureus* but not *E. coli* (**Table 1**). As expected, the presence of a quaternary ammonium on cationic porphyrin enhanced its bactericidal properties, that were also observed in the dark. High efficiencies were also obtained with neutral porphyrins whereas no antibacterial effect were measured anionic derivatives, probably due to its low interaction with negatively-charged bacterial surface[196, 197]. Similar results were obtained using paper as support[198] (**Figure 7**). Interestingly, photo-bactericidal Porphyrin-Cellulose Nanocrystals (CNCs), were also prepared following a similar strategy[199]. A comparison of porphyrin-grafted paper and CNCs evidenced the major influence of the nature of the cellulose materials related to the affinity of the bacterial strain for the surface[198].

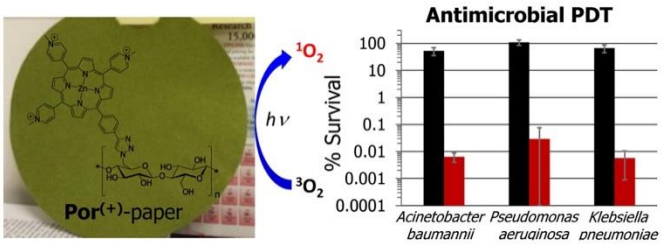


Figure 7. Photoactive coatings based on porphyrin: a cationic porphyrin is grafted on paper *via* a 1,3,5, triazine covalent bond. Generation of ROS under visible light irradiation confers high antibacterial activity to the modified paper. Reprinted with permission from reference 198. Copyright (2015) American Chemical Society

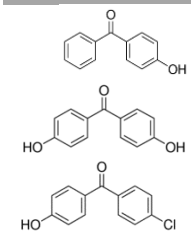
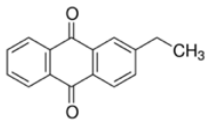
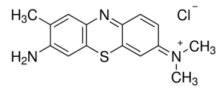
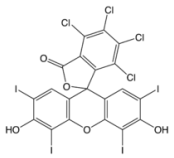
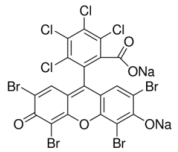
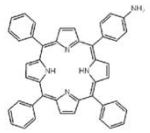
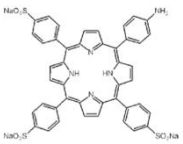
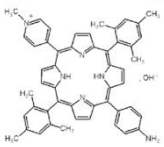
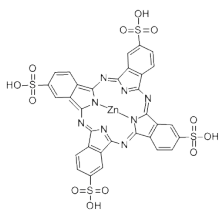
Besides cellulose-based materials, other biopolymers, such as chitosan, gelatin, poly-lysine and poly(3-hydroxybutyrate) have been used as a support for porphyrins[200-205]. For example, Sodium Magnesium chlorophyllin and sodium copper chlorophyllin have also been entrapped in gelatine to create photo-bactericidal edible films, with glycerol added as a plasticizer[202]. Coatings have shown excellent efficiency on *S. aureus* and *L. monocytogene*, but none on *E. coli* and *Salmonella*. Optimization has been performed by varying light intensity and time of irradiation, which revealed to be the most influential parameter for cytotoxicity.

Phthalocyanines are also tetrapyrrole derivatives which have often been compared with porphyrins[206-208]. However, because of their hetero-atomic nature, these photosensitizers mainly absorb in the near-infrared light absorption (630-720 nm), which represents a great advantage for medical applications, as this wavelength range can penetrate deeply in the tissues[209]. As an example, George et al. reported the synthesis of a four-pyridyl substituted phthalocyanine, its Zn complex and tetracationic derivatives, and its impregnation in filter paper[210]. The dipping process created sufficiently strong binding between PS and substrate to avoid leaching. Their photo-bactericidal activity against Gram-negative *E. coli* and *Acinetobacter baylyi* was demonstrated. In this study,

phthalocyanines showed higher efficiency than parent porphyrins. More specifically, the cationic derivative showed the best results in antibacterial tests, probably thanks to favourable interaction with negatively charged bacterial surfaces. Bonnett et al. also compared porphyrins and phthalocyanines, which have been immobilized on nylon-reinforced chitosan films through different methods: adsorption for 5,10,15,20-tetrakis(p-hydroxyphenyl)-porphyrin, dissolution and casting for 5,10,15,20-tetrakis(p-aminophenyl)-porphyrin, and covalent attachment for zinc(II) phthalocyanine tetrasulfonic acid, ZnPcS[206]. This covalent binding, a sulfoamido linkage, is necessary because this latter PS is soluble in water, contrary to studied porphyrins. All these derivatives have shown good photo-bactericidal effect against *E. coli* (**Table 1**). Not only did phthalocyanine derivative show the best results as antibacterial agent, but the grafted membrane was still effective after 9 months of conservation in the dark.

As a summary, incorporation of photosensitizers in bio-sourced polymer-based materials has been widely explored. Most of them do not release the photosensitizer, but trap it onto or into the matrix, constituting a solid or gel material whose anti-bactericidal effect mostly originates from light-induced ROS production. Despite the short lifetime of ROS, very promising results have been accumulated. Many parameters can influence the photo-bactericidal activity of PS, including hydrophilicity, side groups, light intensity and exposure time, and metal complexation for macrocycles. The photo-bactericidal efficiency is generally higher against Gram positive than Gram negative bacteria, probably due to difference in membrane structure. Resulting coatings can be resistant to washes and/or stable over long periods of time. Some of the reported systems are efficient even against antibiotic-resistant strains, which suggests a bright future for their use in photo-dynamic treatments.

Table 1. Examples of photosensitizer-based bio-sourced antibacterial coatings

Photosensitizer	Support	Method of incorporation	Light source	Antibacterial activity: *Bacterial strain* (reduction rate)	Exposure time	Refs
 4-hydroxybenzophenone 4,40-dihydroxybenzophenone 4-chloro-40-hydroxybenzophenone 4-benzoylbenzoic acid	Cotton fabrics	pad-dry-cure method	UV (365 nm) 1.85 mW.cm^{-2}	*S. aureus* / *E. coli* (>99.999% / 99.997%) (99.998% / 99.665%) (99.909% / 98.903%) (88.696% / 68.387%)	1 h	149
 2-ethylanthraquinone	Cotton fabrics	Vat dyeing process	UVA (385nm) 30 mW/cm^2	*S. aureus* / *E. coli* (99.99% / 99.99%)	1h	154
  Toluidine blue O + Rose Bengal	Cellulose acetate	Solvent evaporation	28 W fluorescent Visible light 3,700 Lux	*S. aureus* (99.6%/100%) MRSA (100%) *E. coli* (24%/100%) *C. difficile* (100%) *C. albicans* (88%)	2/6 h 6 h 6/16 h 4 h 16 h	189
 Phloxine B	Cellulose/PVA	Layer-by-layer process	White light 0.45 mW.cm^{-2}	*P. aeruginosa* (> 99.5%) *L. monocytogene* (> 99.5%) *B. anthracis* (> 99.5%) *S. Typhimurium* (< 10%) *E. coli* (< 10%)	30 min	179
 **Tetraphenylporphyrin** Neutral  Anionic  Cationic	Cotton	1,3,5-triazine covalent binding	LED model Luxeon Star White 9.5 J.cm^{-2}	*E. coli* / *S. aureus* (0 % / 93.7 %) (0% / 37 %) (0 % / 100%)	24 h	196
 Zinc(II) phthalocyanine tetrasulfonic acid tetrasodium salt	Chitosan	Sulfo amido covalent grafting	Halogen lamp n° CY-118A, 500 W, 230 V, 50 Hz	*E. coli* (> 2 logs)	160 min	206

3.2. Dual Role of Dyes as Photosensitizers for Photo-Polymerization and Photo-Inactivation of Bacteria.

Elaborating on the two above-described approaches, the possibility to use dyes as photosensitizers both for initiating the photopolymerization process and as ROS generators for aPDT was also studied. Once the dyes are incorporated in the photoinduced and reticulated polymer material, the visible light activation of the material may generate on its surface biocide ROS species responsible for the death of bacteria. In this respect, natural resources can be valorised as monomers, just as discussed previously, but also as promising photo-initiating systems: natural dyes compete with synthetic ones for initiation of polymerization under visible-light activation[211, 212].

Curcumin derivative-coatings prepared on stainless steel substrates after the cationic epoxy polymerization of epoxidized soybean oil under light irradiation demonstrated antibacterial efficiency with and without visible light irradiation[213]. Curcumin/iodonium salt photoinitiating system was used to perform the cationic photopolymerization (CP) and curcumin played also the role of singlet oxygen promoter. The cross-linking reaction was efficient enough to hinder curcumin release from the coatings over several hours in water. Under visible light exposure, these coatings led to a strong reduction of *S. aureus* and *E. coli* by 99% and 95%, respectively, after 48h of incubation. Similar antibacterial results were obtained with eosin Y[176] and quercetin[214] Recently, new photoactivable, environmentally-friendly and antibacterial coatings were prepared from paprika which efficiently promoted the CP of a bio-sourced and renewable monomer, gallic acid, in a reduced time.[42] A remarkable decrease by 100% of *E. coli* and *S. aureus* on the surface of the gallic-acid/paprika derived coatings was observed under visible-light illumination, without any remaining live bacteria after 6h (**Figure 8**).

Interesting analogues of classical photoinitiators can also be found among plants components, such as flavonoids or quinone derivatives. For instance, quercetin could play a dual role of photoinitiator and photobactericidal agent when incorporated in a glycerol triglycidyl ether matrix[214]. Iodonium salt was again used as co-initiator for the near-UV induced cationic polymerization of this oil monomer. Antibacterial properties of the photoinduced materials were evaluated: while successful inhibition of Gram-positive bacteria was emphasized after only 2h of irradiation (99% inhibition of *S. aureus*), antibacterial effect against Gram-negative *E. coli* could not be observed.

A well-known dye extractable from madder root, purpurin, was also studied in a similar purpose[215]. Combination of purpurin derivatives with Iod successfully lead to the free-radical polymerization of epoxidized acrylate soybean oil both under air or in laminate. Materials synthesized from purpurin-

based initiating systems demonstrated encouraging photobactericidal properties against *S. aureus*. Interestingly, the dye was functionalized with allyl moieties, bringing two advantages compared to previous works: (1) functionalization significantly improves initiating properties of the dye, by preventing inhibition of radicals by phenols; (2) the co-polymerization of the dye in the polymer matrix permits to prevent its leakage, thus enhancing stability of the film properties. Notably, complete inhibition of *S. aureus* could be repeated along three irradiation cycles.

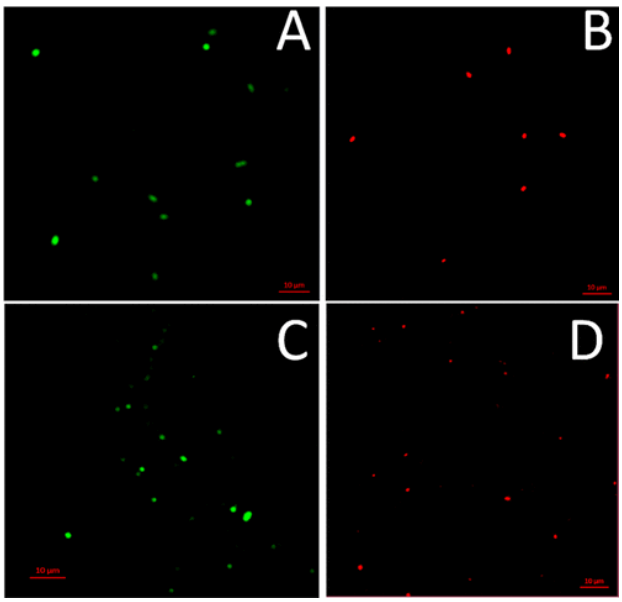


Figure 8. Live/dead assay performed on gallic-acid/paprika derived coatings in the presence of *E. coli* (A, B) and *S. aureus* (C, D), before (A, C) and after (B, D) visible light irradiation[42]. Reprinted with permission from [https://pubs.acs.org/doi/10.1021/acssuschemeng.7b03723]. Copyright (2018) American Chemical Society.

Such a use of dyes as PS for both photopolymerization and antibacterial PDT perfectly addresses both current green chemistry and medical challenges. In particular, the huge advantage of the photo-bactericidal mechanism compared to other antibacterial strategies is that no bacterial resistance is expected[216]. However, an efficiency/toxicity balance needs to be found to prevent the detrimental effect of ROS on mammalian cells. Besides, it remains often necessary to associate natural dyes with other non-bio-sourced molecules as co-initiator. The development of fully bio-based and non-toxic photo-initiating systems, synthesizable through green processes, still remains a challenge.

4. Conclusions and perspectives

As an answer to the increasing phenomenon of resistance against antibacterial treatments in hospitals, novel strategies are rapidly developing, and scientists have vied with each other in ingenuity to develop effective antibacterial materials. In this context, the development of green antibacterial

materials *via* photochemical methodology appears particularly relevant. Photochemistry has several key advantages over other synthetic approaches as it allows the manipulation of sensitive bio-compounds and permits fast and efficient reactions, with a fine spatiotemporal control, and does not require heat or any solvents. This field progresses in symbiosis with green organic chemistry, which highlights the huge potential of natural compounds (terpenes, polyphenols, polysaccharides, …) as cheap, renewable, and safe base material. Judicious combination of light and bioresources could be the key to efficiently answer the challenge of bacterial resistance. When bioresources offer a rich library of antibacterial agents, such as essential oils or peptides, photochemistry enlarges the spectrum of weapons with *in-situ* generation of nanoparticles and photodynamic therapy. In addition, PDT seems exempted from the thread of bacterial resistance[216]. As a matter of fact, current antibacterial strategies consider that combining complementary antibacterial methods is the best alternative to overcome their innate defences[217]. Association of complementary antibacterial agents, with for instance contact-killing and photobactericidal activities, is now reachable through fast one-step photochemical process. Abundancy of options to be explored in this field, supported by the burst of interest in photochemistry and green chemistry this last decade, could accelerate the development of long-term and effective antibacterial materials. However, in photochemical process, chemical modifications or introduction of additives are generally necessary, which need to be considered for biocompatibility issues. Answers to this limiting point are emerging, such as replacing potentially toxic photoinitiators by natural dyes, which also cope with green chemistry requirements. The development of new water-based photoinitiating systems or formulations preventing the need and release of organic compounds should also be privileged. In agreement with progresses of photopolymerization technologies, efforts are also being made to switch irradiation conditions to visible-light or NIR[218] to avoid harmful effects of classical UV-sensitive systems, and to penetrate deeper in tissues[51]. The use of two-photon (2P) absorption is also perfectly well-adapted to the elaboration of innovative antibacterial materials upon near-InfraRed or InfraRed irradiation, as recently demonstrated with curcumin[219]. This new concept focuses on the pivotal role of the natural dye as 2P free-radical photoinitiators and photogenerators of ROS, combined with judicious nanometric and micrometric topographical strategy: 3D µ-cages were designed to entrap and rapidly kill bacteria upon visible-light exposure. Another interesting approach would lie in the use of sunlight and natural sources of light-emission properties (*i.e.* bioluminescence), an option that, to our knowledge, has never been explored so far.

Last but not least, contributions of photopolymerization in the medical field are multiple, and have exploded with the development of 3D-printing technologies. Its applications are not anymore limited

to surface coatings or wound healing: high-resolution prosthetics for dentistry or tissue engineering can now be generated on demand. Surprisingly, although photochemistry-based processes have been widely developed for the preparation and patterning of 3D hydrogels[220], there are only very few reports dedicated to their antibacterial applications[221, 222]. One particularly interesting and challenging research area is the development of cellularized hosts for tissue engineering since very few photochemical processes are so far compatible with cell encapsulation[223].

Conflicts of interest

There are no conflicts to declare

Acknowledgements

Dr. Davy-Louis Versace would like to thank French National Research Agency (ANR, sPECTRAL project), University Paris-Est Creteil (UPEC) and Institut de Chimie et des Matériaux Paris-Est (ICMPE) for financial support. We also would like to thank Pauline Sautrot-Ba for her participation and Dr. C. Hélary (LCMCP) for his contribution to the fruitful collaboration between Davy-Louis Versace and Thibaud Coradin over the last years.

Abbreviations

aPDT antibacterial Photodynamic Therapy, AMP Antibacterial Peptide, AQ Anthraquinone, BP Benzophenone, BTCA 1,2,3,4,-butanetetra carboxylic acid, BPTCD 3,3,4,4-benzophenonetetracarboxylic dianhydride, CC cyanuric chloride, CDI N,N'-carbonyldiimidazole, CFU Colony Forming Units, CNCs Cellulose Nanocrystals, CQ Camphorquinone, DMAE 2-Dimethylaminoethanol, DMAEMA 2-(dimethylamino)ethyl methacrylate, E. coli Escherichia coli, EPR Electron Paramagnetic Resonance, ELP Elastin-like polypeptide, EOs Essential Oils, EY Eosin Y, FDA Federal Drug Administration, HA Hyaluronic Acid, ISC Inter-System Crossing, LEDs Light Emitting Diodes, MB Methylene Blue, MIC Minimal Inhibitory Concentration, MRSA Methicillin-Resistant Staphylococcus aureus, mTCPP 4,4',4'',4'''-(porphine-5,10,15,20-tetrayl)tetrakis(benzoic acid), NP nanoparticles, PDT Photodynamic Therapy, PEG Poly(ethylene glycol), PEGDA Poly(ethylene glycol) diacrylate, PEI Poly(ethylene imine), PHAs Poly(hydroxyalkanoates), PHBHV poly(hydroxy-butyrate-hydroxy valerate), PI photoinitiator, PLA Poly(lactic acid), PpIX Protoporphyrin IX, PS Photosensitizer, QA Quaternary Ammonium, QP Quaternary Phosphonium, RB Rose Bengal, ROS Reactive Oxygen Species, SSI Surgical Site Infections,

S. aureus Staphylococcus aureus, TBO Toluidine Blue O, TMPTMA Trimethylolpropane trimethacrylate, TMPTMP Trimethylolpropane tris(3-mercaptopropionate), TPP Triazinylporphyrin, UVA UltraViolet A, 4VP 4-vinylpyridine, ZnPcS Zinc(II) phthalocyanine tetrasulfonic acid.

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