Photocrosslinkable Antimicrobial and Antiviral Polymers for Modification of Textiles

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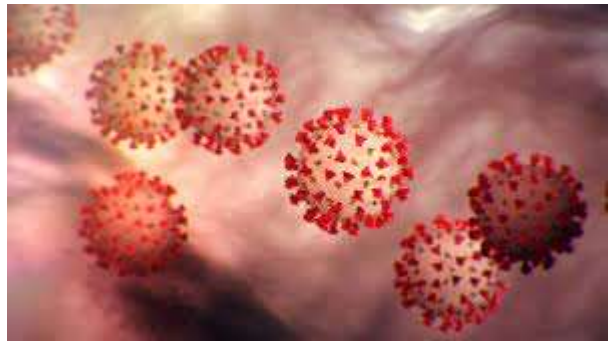
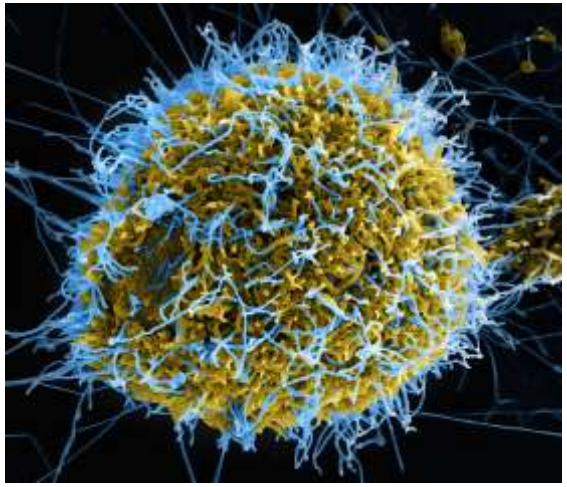
Contaminated surfaces result in hospital-acquired infections that cause almost 100,000 deaths each year in the US.

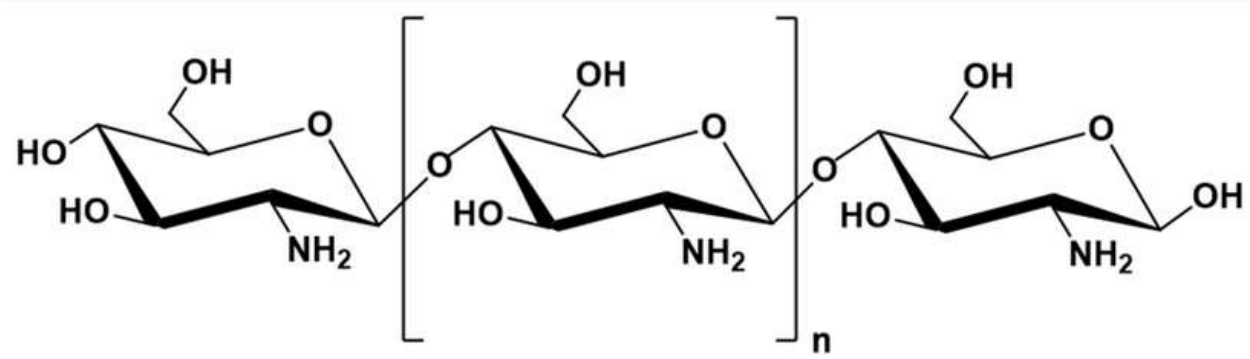
Surfaces and materials that can inhibit/kill pathogens to address disease transmission are needed.

Antimicrobial/antiviral surfaces include those based on metal nanoparticles, nanoscale patterning, hydrophobic coatings, and amino- or phosphino-polymers.

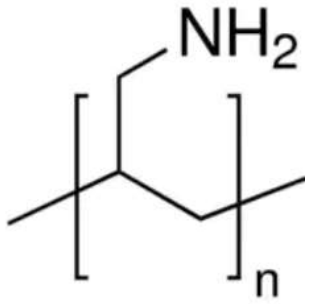




Primary amine containing polymers



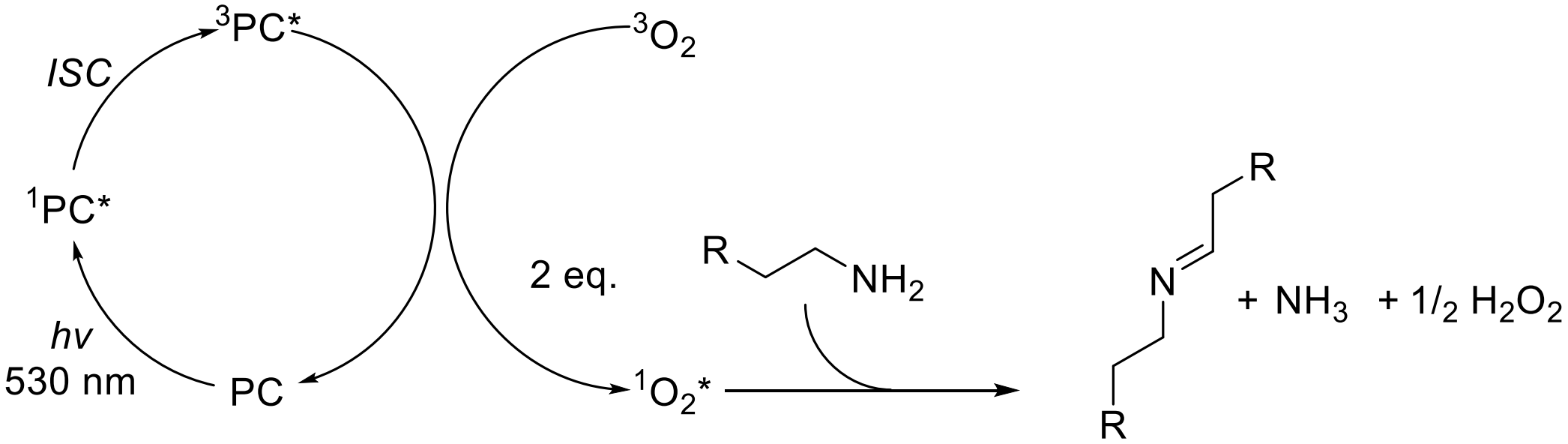
Chitosan



Polyallylamine

- Widely explored as antibacterial textile and surface coatings
- Issues: **water solubility, prohibitive cost, or poor mechanical properties resulting from a lack of chemical cross-linking**
- Crosslinking antimicrobial polymers to enhance durability while maintaining mechanical properties, and reducing leaching into aqueous environments is an attractive approach to improved coating materials

Photocatalytic amine coupling to give imine crosslinks

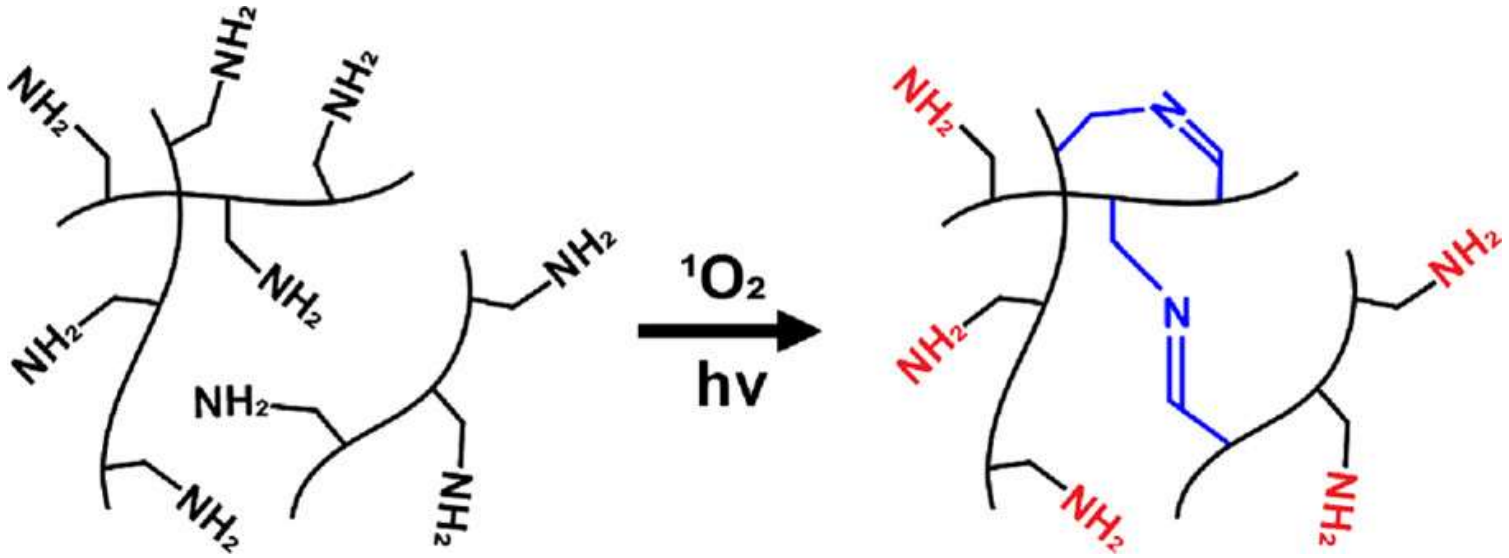


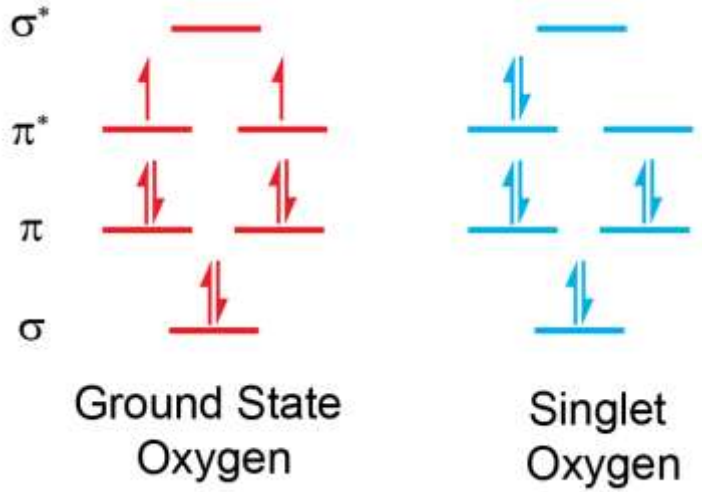
Reaction can be controlled with amount of light and sensitizer

Amines to imines with small molecule byproducts

Chen, B.; Wang, L.; Gao, S. *ACS Catal.* **2015**, *5*, 5851–5876
Ho, R.Y.; Liebman, J.F; and Valentine, J.S. *Active Oxygen in Chemistry;* Springer, **1995**

Photochemical crosslinking of amino-functionalized polymers is an approach to obtain robust coatings

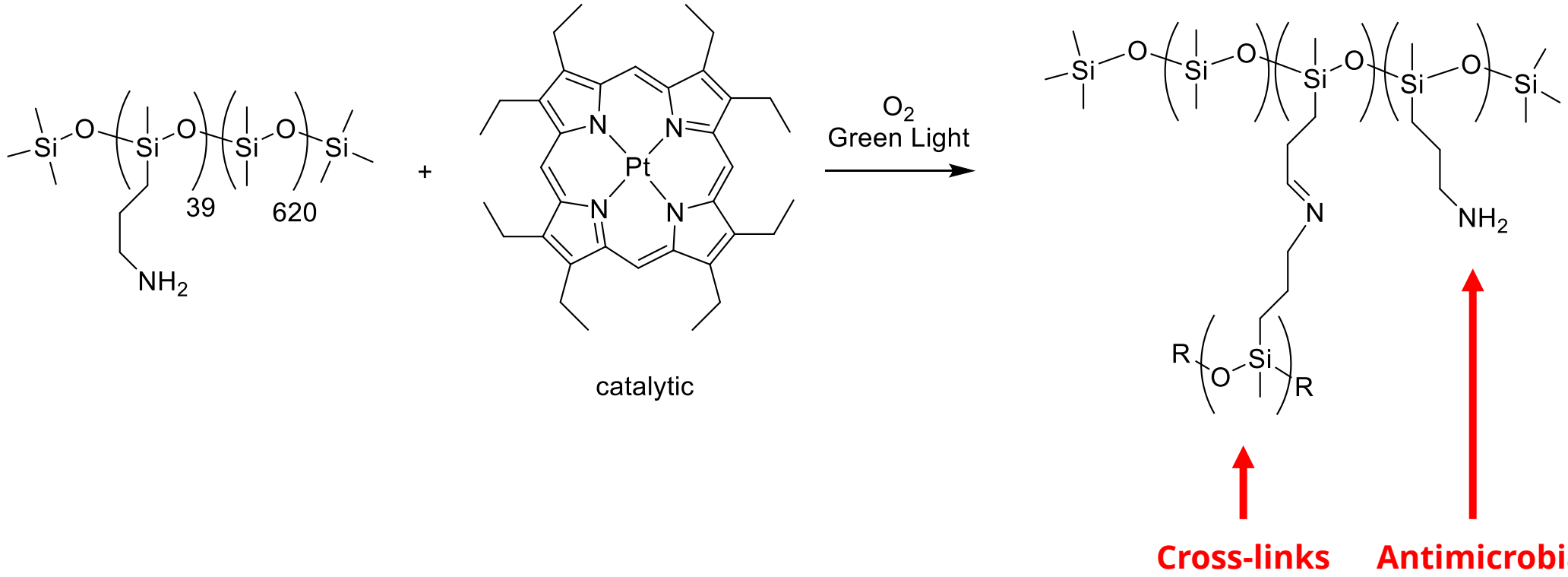




$^1O_2$ is a strong oxidant

Similar to ozone, peroxides, etc (ROS)

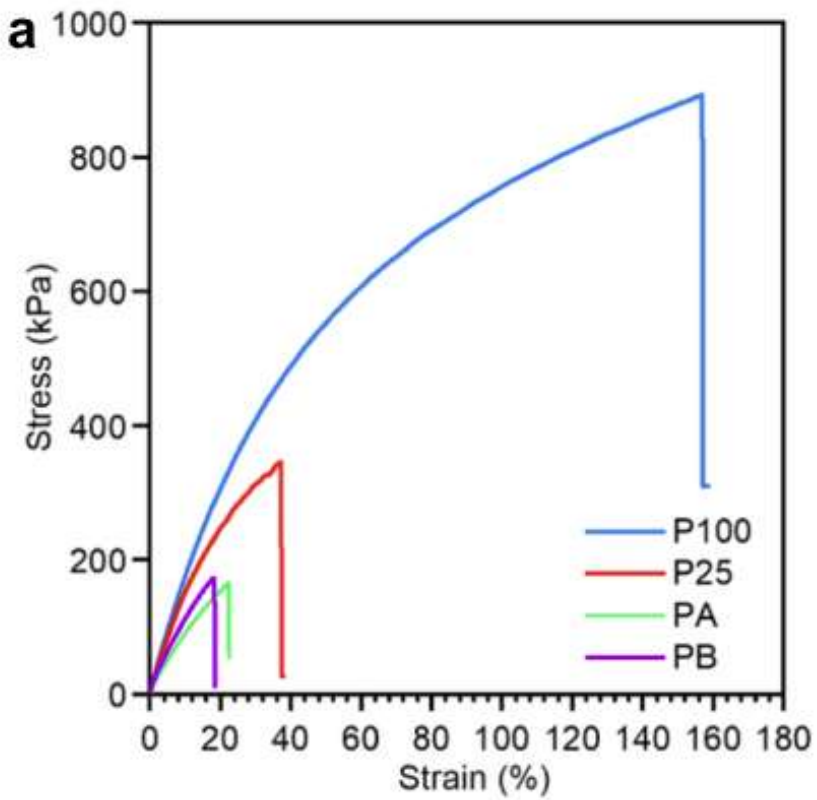
Oxidative photo-cross-linking of amine containing copolymers

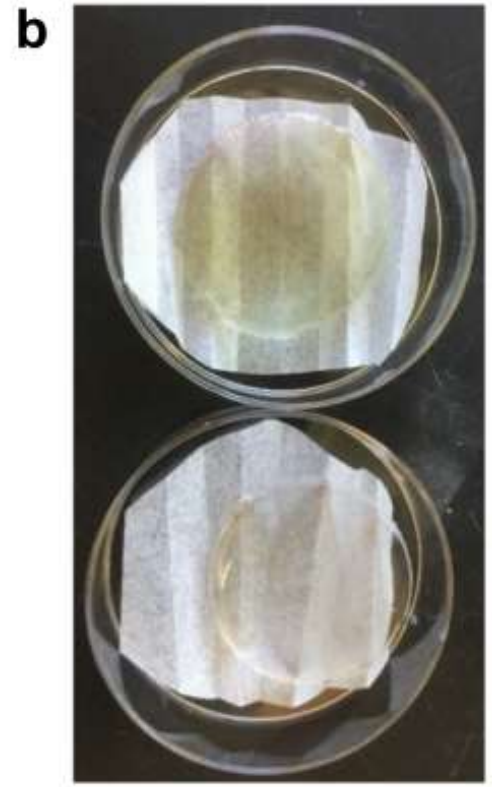


Wright, T.; Tomkovic, T.; Hatzikiriakos, S. G.; Wolf, M. O. *ACS Appl. Polym. Mater*. **2020**, 2, 4802-4808.

Characterization

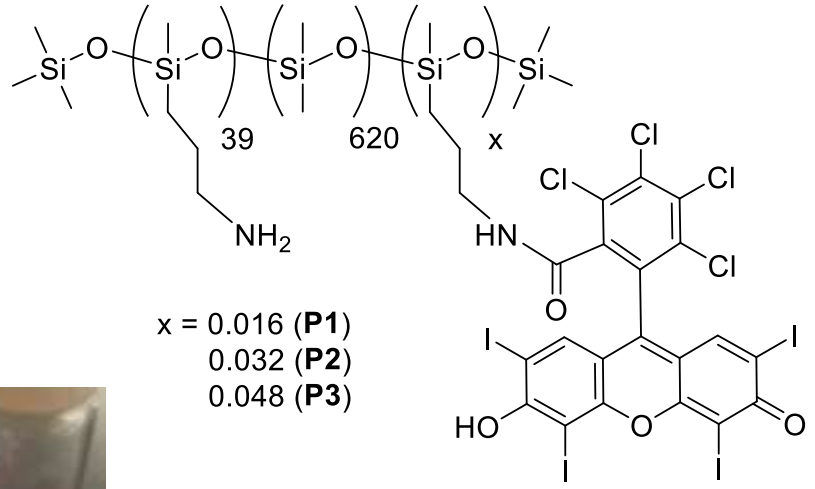
Mechanically Robust



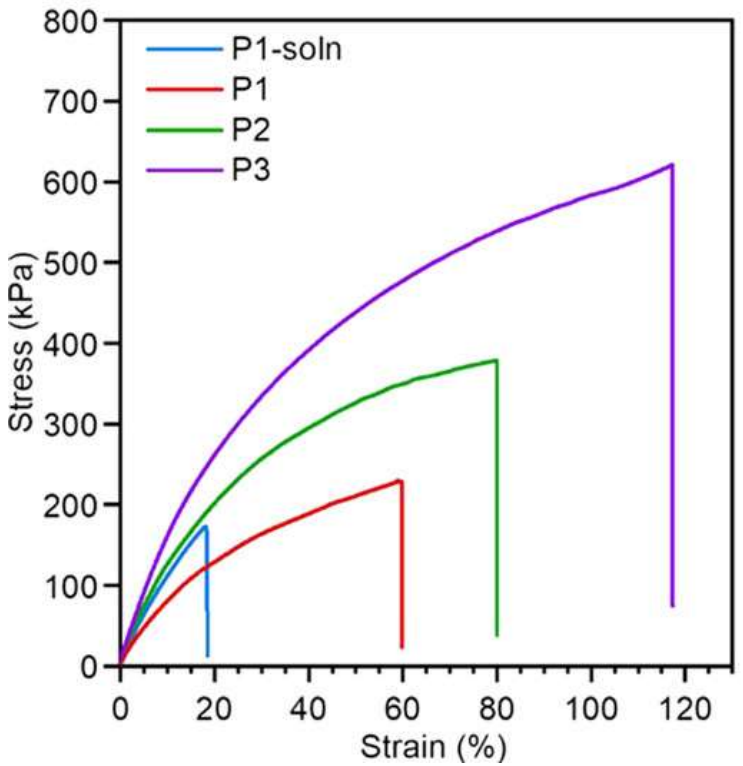


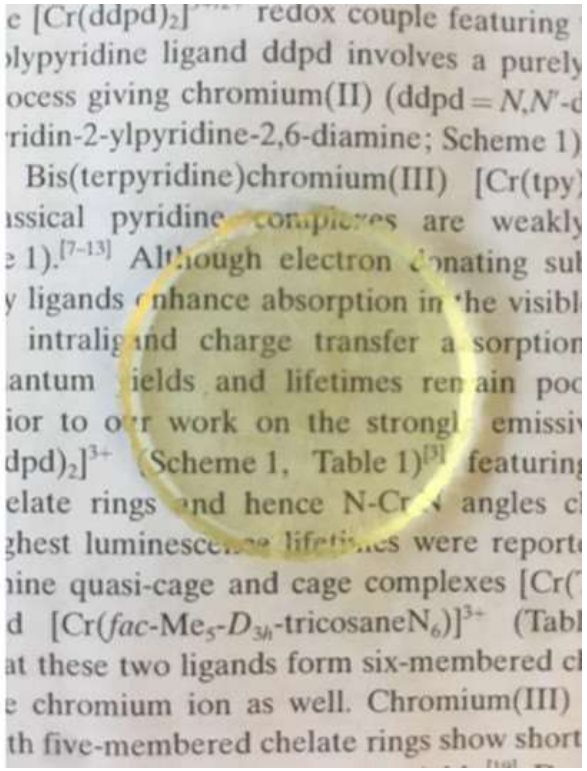
Collaboration with Alshakim Nelson and Dylan Karis, University of Washington

Single component system



ROSE BENGAL



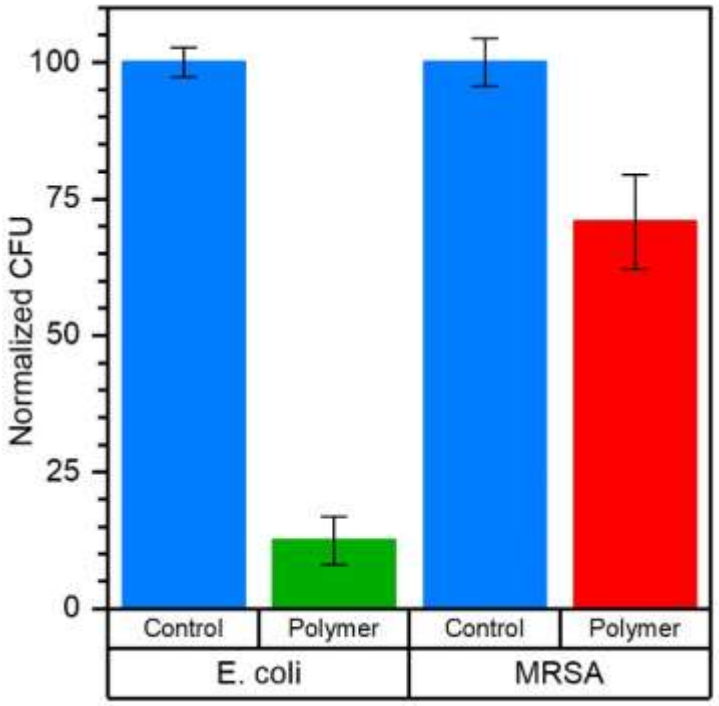

e [Cr(ddpd)$_2$] redox couple featuring
olypyridine ligand ddpd involves a purely
ocess giving chromium(II) (ddpd = *N,N'*-d
ridin-2-ylpyridine-2,6-diamine; Scheme 1)
Bis(terpyridine)chromium(III) [Cr(tpy
assical pyridine complexes are weakly
e 1).[7–13] Although electron donating sub
y ligands enhance absorption in the visibl
intralig and charge transfer a sorption
antum ields and lifetimes ren ain poo
ior to our work on the strongl emissiv
dpd)$_2$]$^{3+}$ (Scheme 1, Table 1)[3] featurin
elate rings and hence N-Cr angles c
ghest luminescence lifetimes were report
nine quasi-cage and cage complexes [Cr(
d [Cr(*fac*-Me$_5$-*D*$_{3h}$-tricosaneN$_6$)]$^{3+}$ (Tabl
at these two ligands form six-membered c
e chromium ion as well. Chromium(III)
th five-membered chelate rings show short

Same cross-linking behaviour

Wright, T.; Karis, D.; Millik, S. C.; Tomkovic, T.; Hatzikiriakos, S. G.; Nelson, A.; Wolf, M. O. *ACS Appl. Mater. Interfaces* **2021**, *13*, 22195–22203.

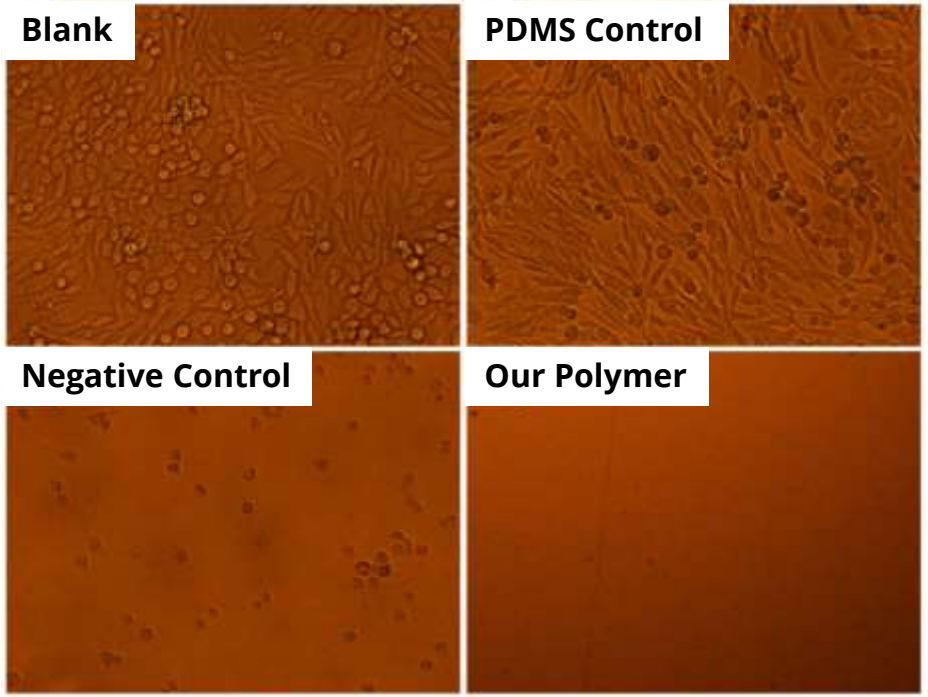
Activity against bacteria and mammalian cells

Bacteria



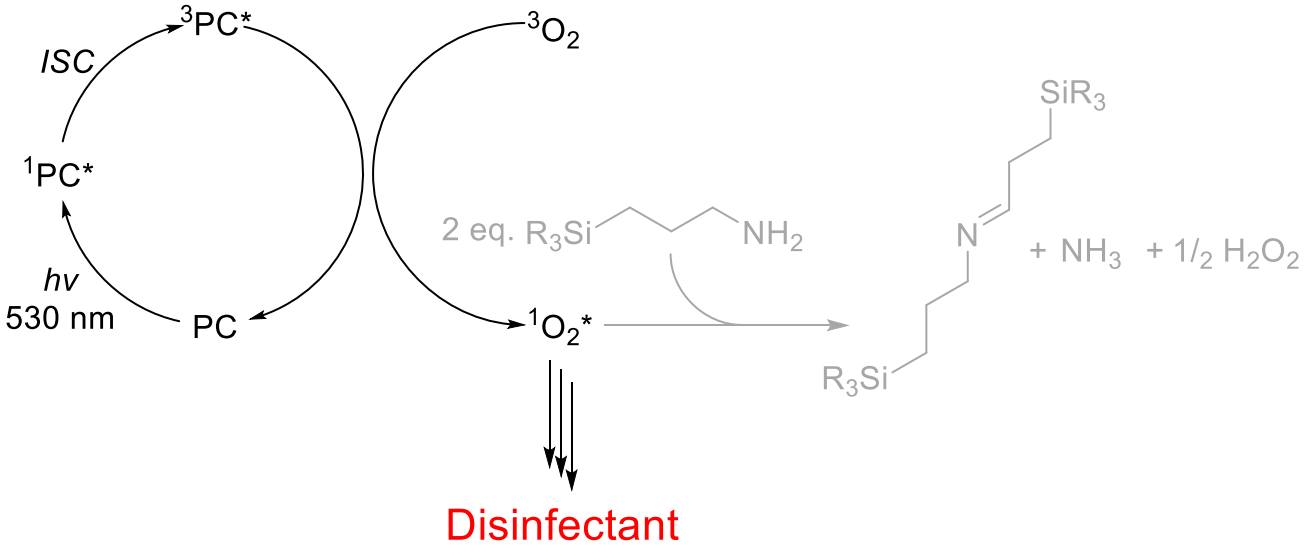
Inverse effectiveness vs chitosan

Mammalian Cells



Material induces complete cell lysis

Singlet oxygen antimicrobial photodynamic inactivation (aPDI)



Effective disinfection vs:

- Bacteria
- Viruses
- Fungi
- Mammalian Cells
- Organic Contaminants

Readily damages cellular components

Pinto, A.; Pocard, M. *Pleura Peritoneum* **2018**, *3*, 1–22
Shen, H. R.; Spikes, J. D.; Smith, C. J.; Kopeček, J. *J. Photochem. Photobiol. A Chem.* **2000**, *130*, 1–6

Modifying Textiles

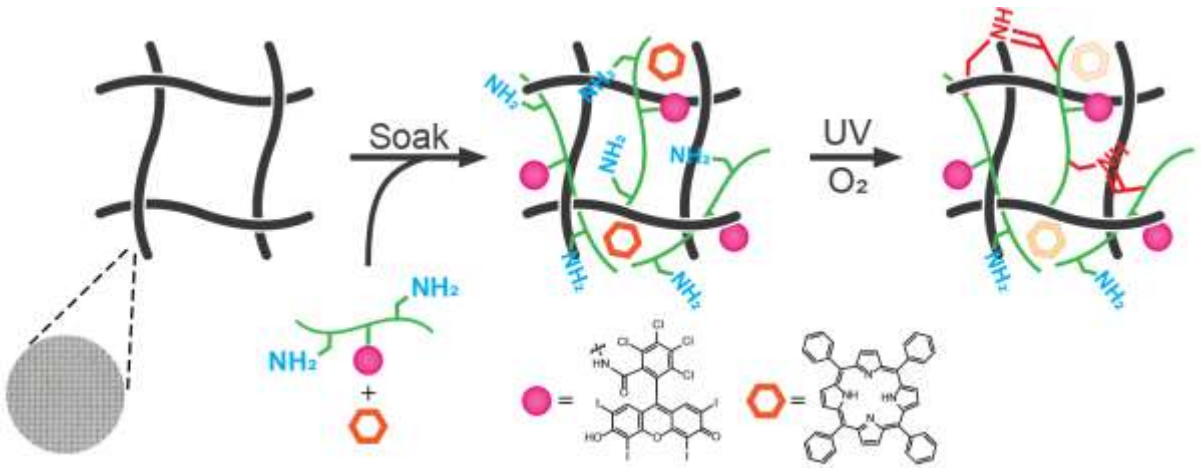
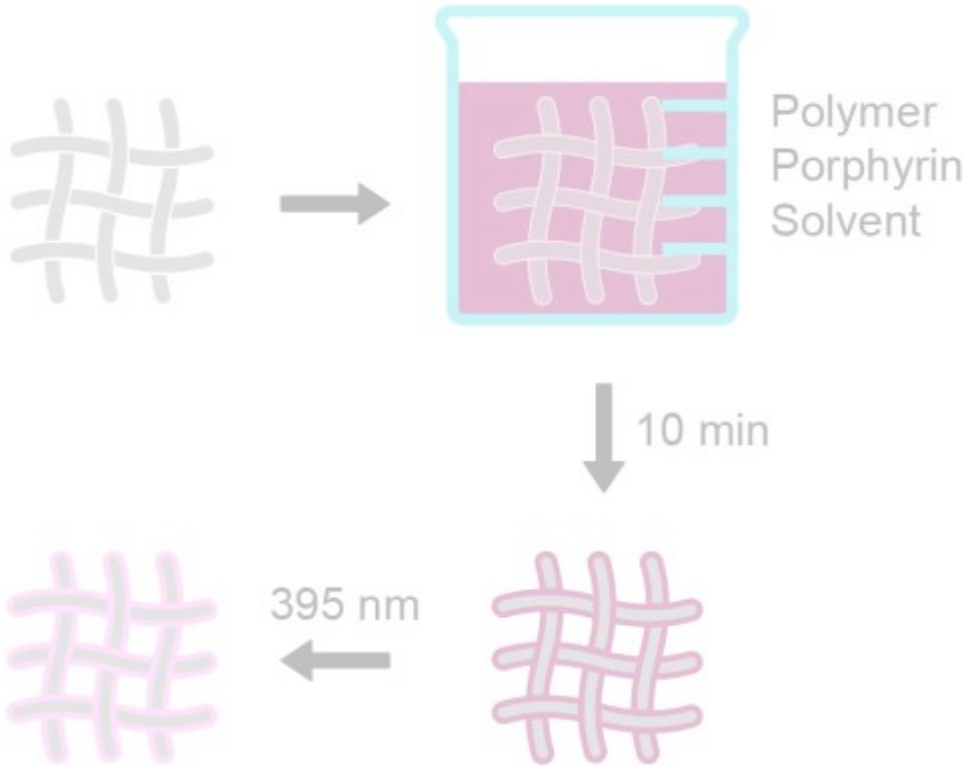


Photo-cross-link polymer onto fabric

Amines kill microbes on contact

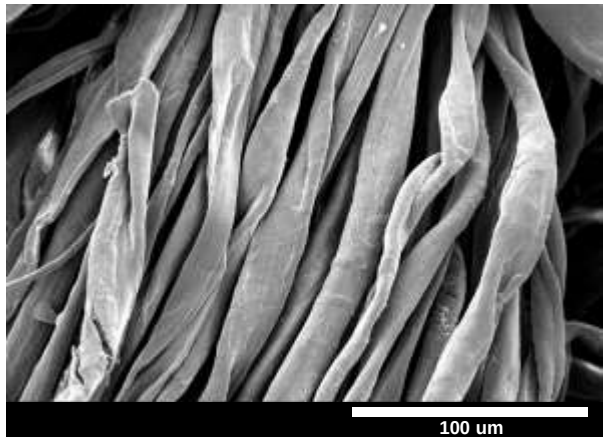
Photo-generate $^1O_2$ for increased activity



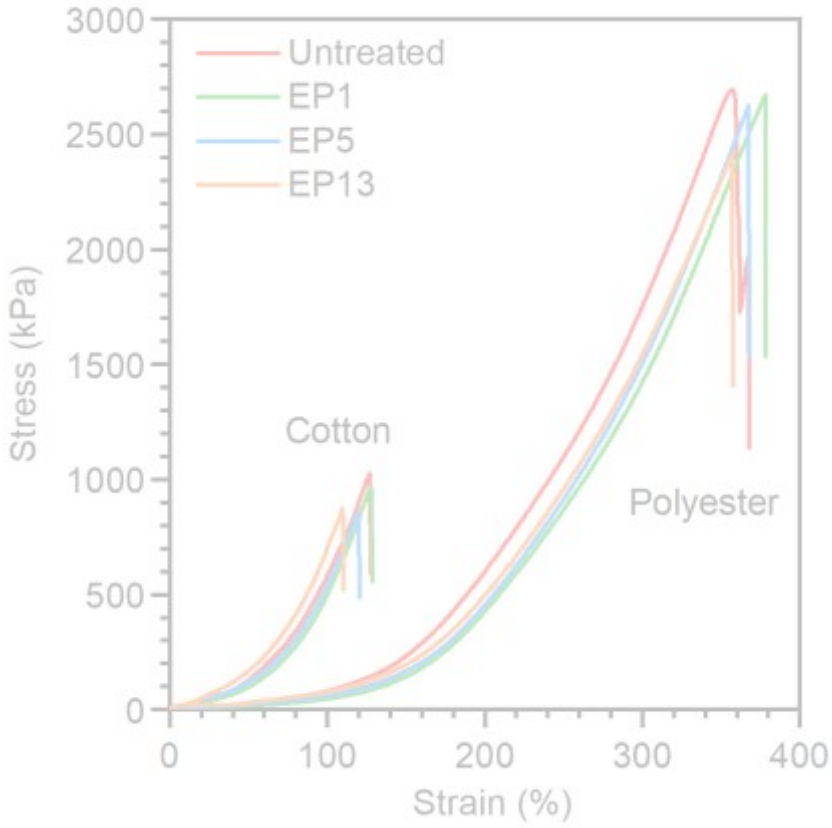
Characterization

Cotton

SEM (500×)



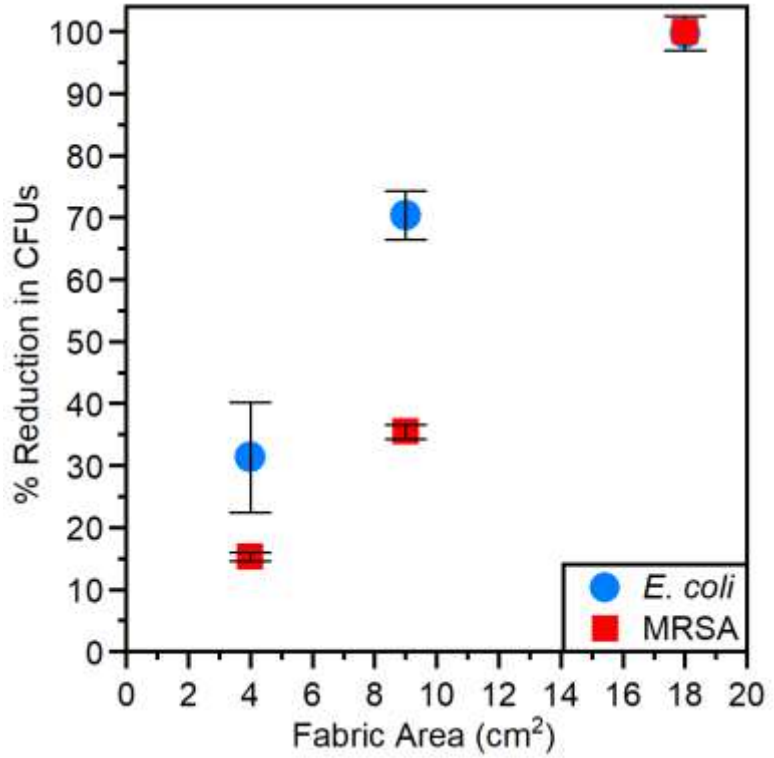
Mechanical Testing



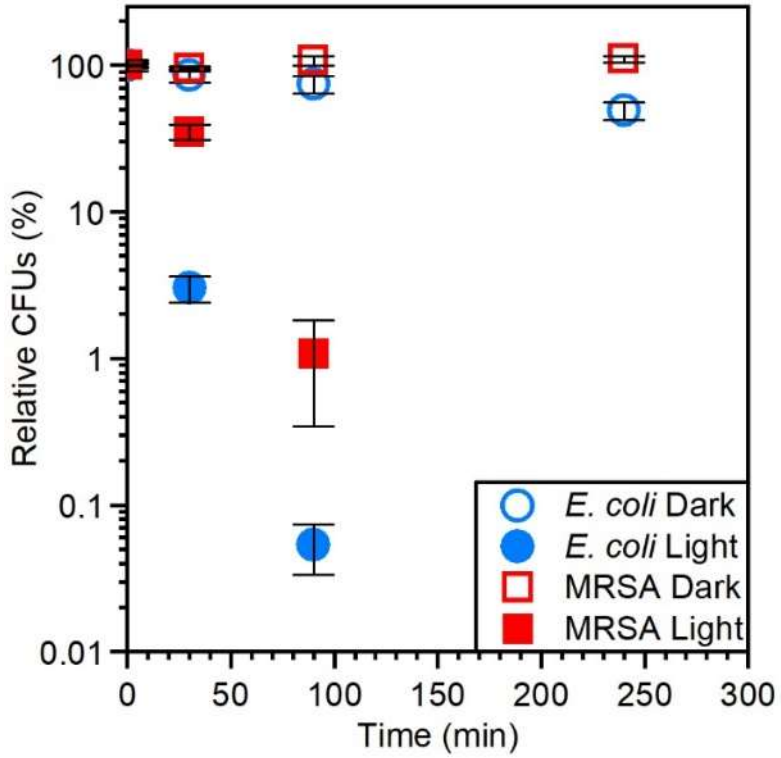
No change in mech properties

Antimicrobial activity

Contact Killing (Dark)



aPDI (Light)

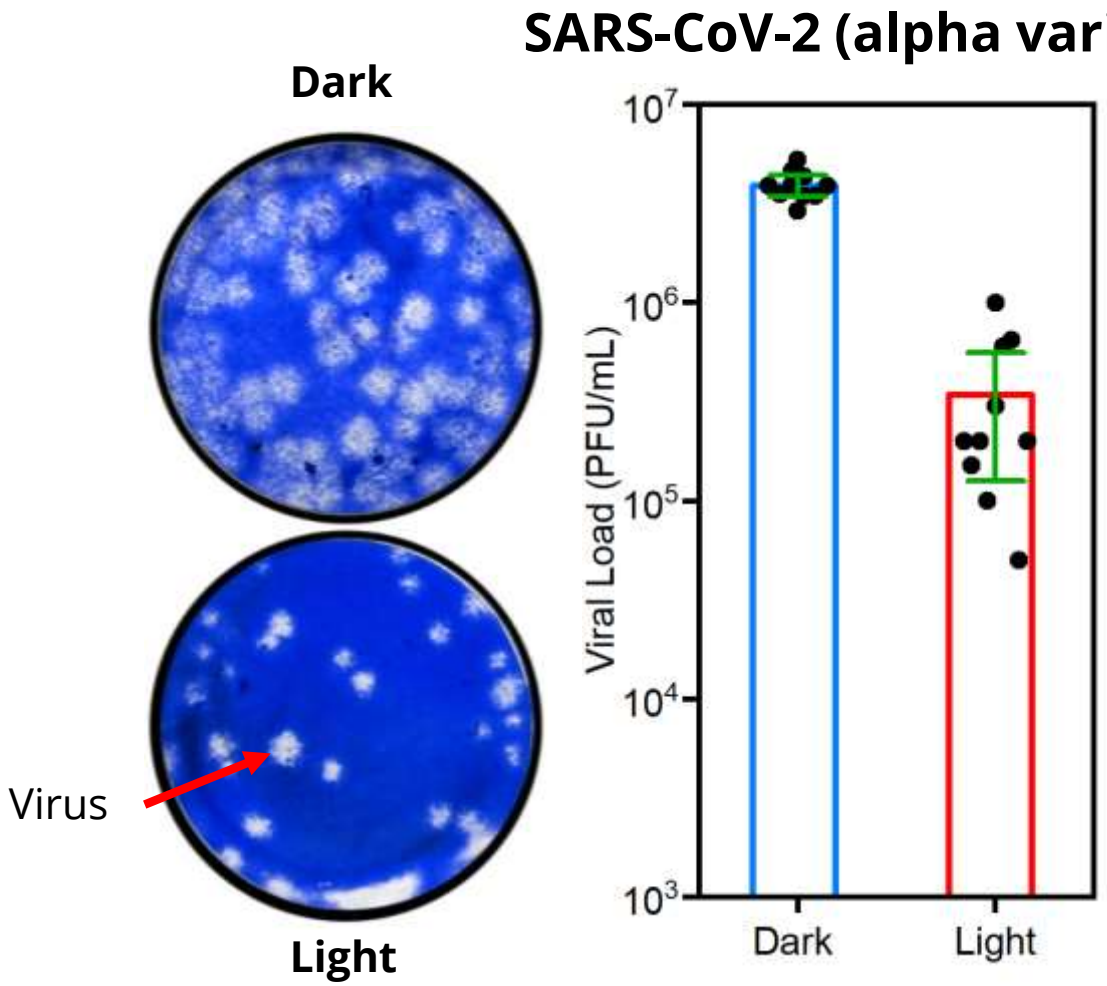


>98% decrease in CFUs after 24 hours

>99.9% decrease in CFUs after 90 minutes

Shorter crosslinking time (5 minutes) results in better antimicrobial activity

Antiviral activity

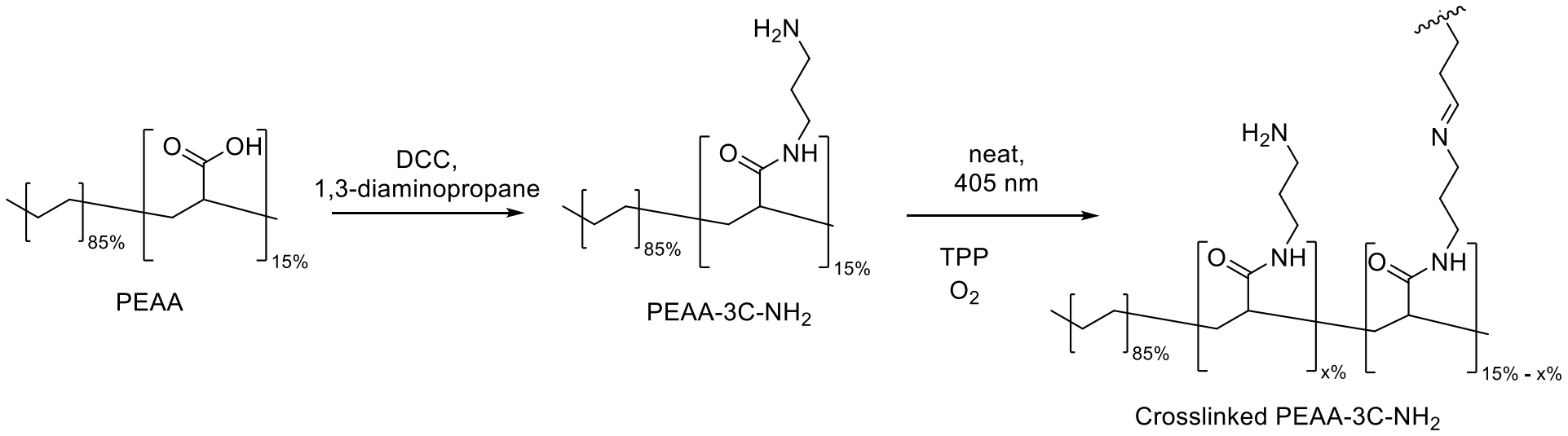


- **Incubate in dark or under 530 nm**
- **Draw samples after 2 hours**
- **Infect into cells, measure**

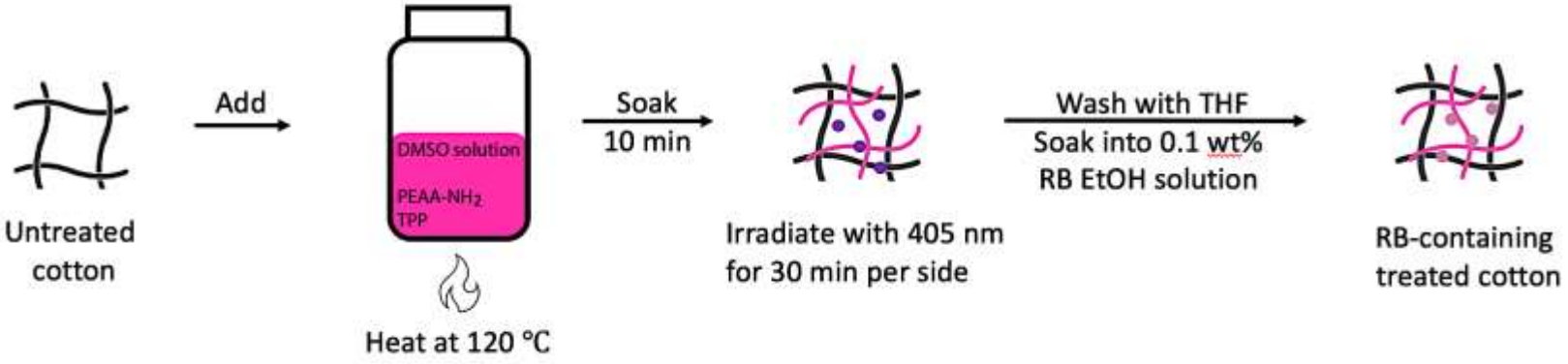
10× decrease in viral load

Tirosh Shapira, Marli Vlok, Andrea Olmstead, François Jean (UBC Microbiology & Immunology)

Photocrosslinking amine terminated poly(ethylene-co-acrylic acid)

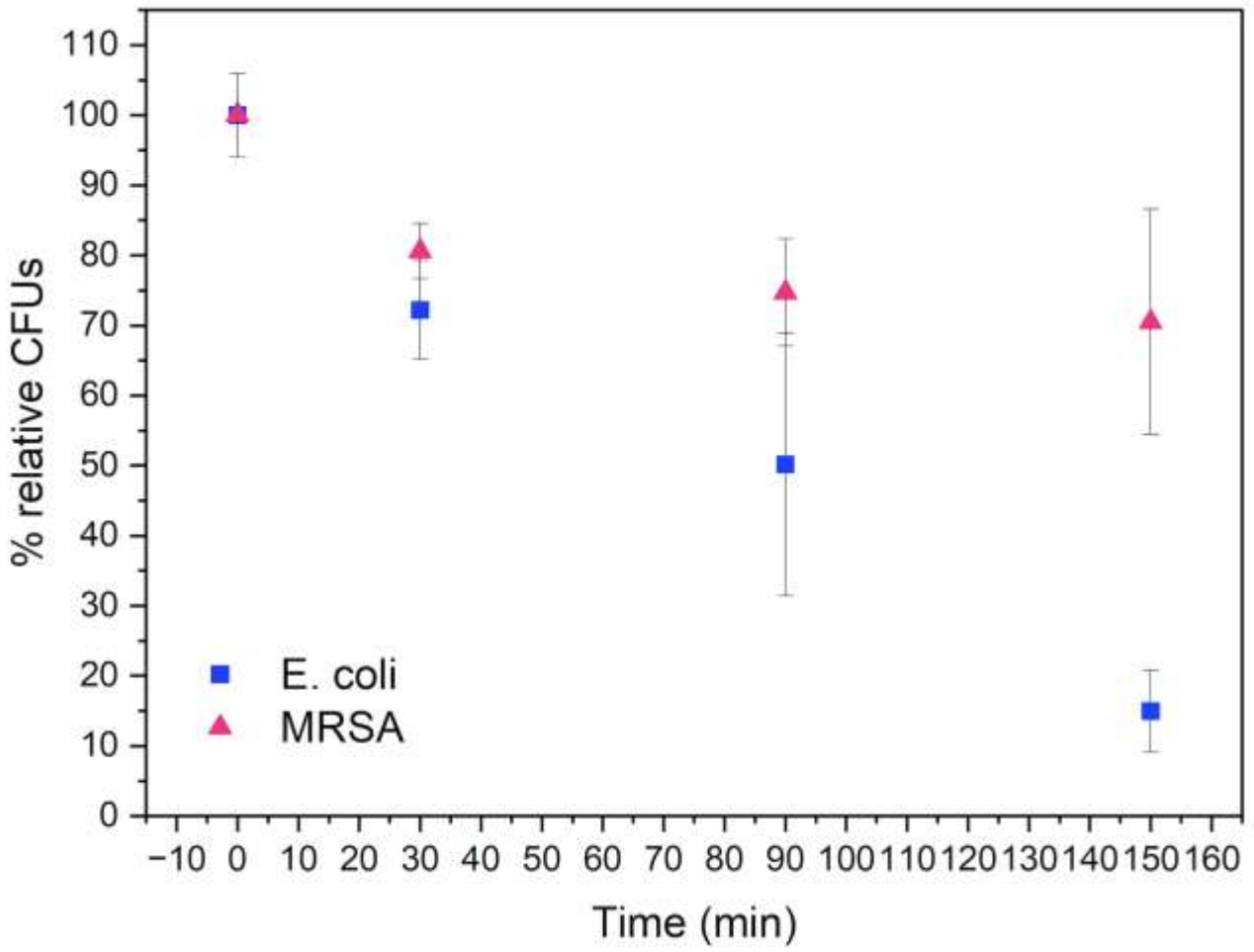


- Photocrosslinked polymer coating on cotton is hydrophilic
- Length of amine linker can be varied



Yimin Zeng

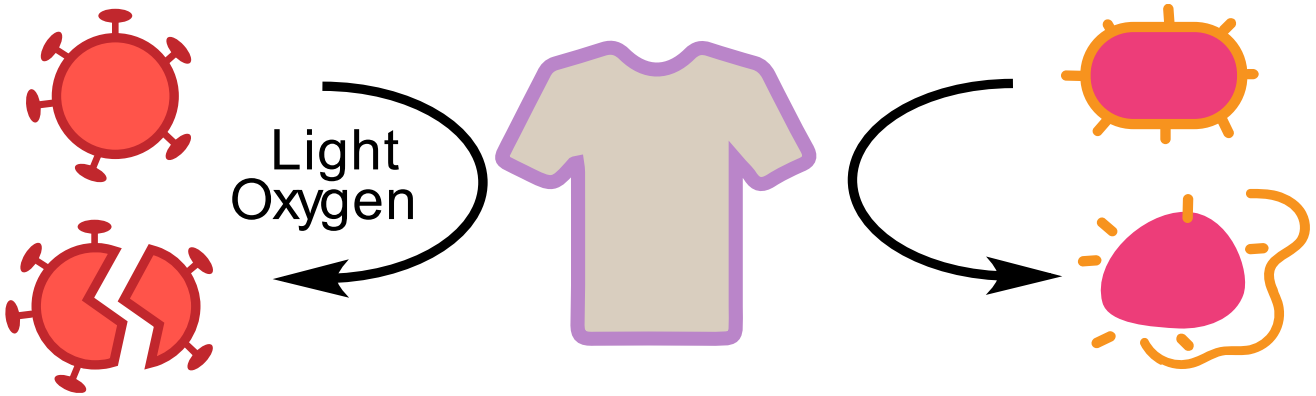
Photocrosslinking amine terminated poly(ethylene-co-acrylic acid)



- All bacteria were killed with green light irradiation (530 nm) within 10 min
- Hydrophilic coating can impart breathability to textile while maintaining antibacterial function

Yimin Zeng

Photocrosslinking of amino-functionalized polymers gives highly effective antimicrobial and antiviral coatings for textiles



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Dr. Andrea Olmstead
Dr. Francois Jean

AMPEL
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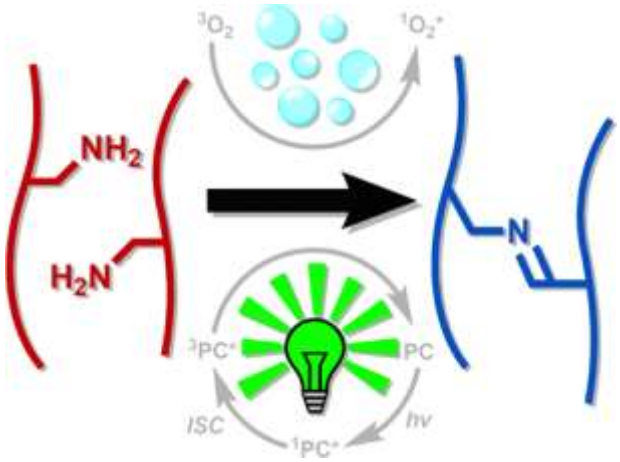
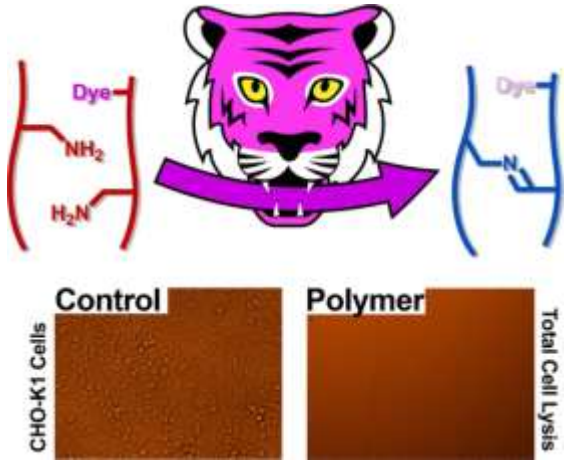
CHAPTER 4+5

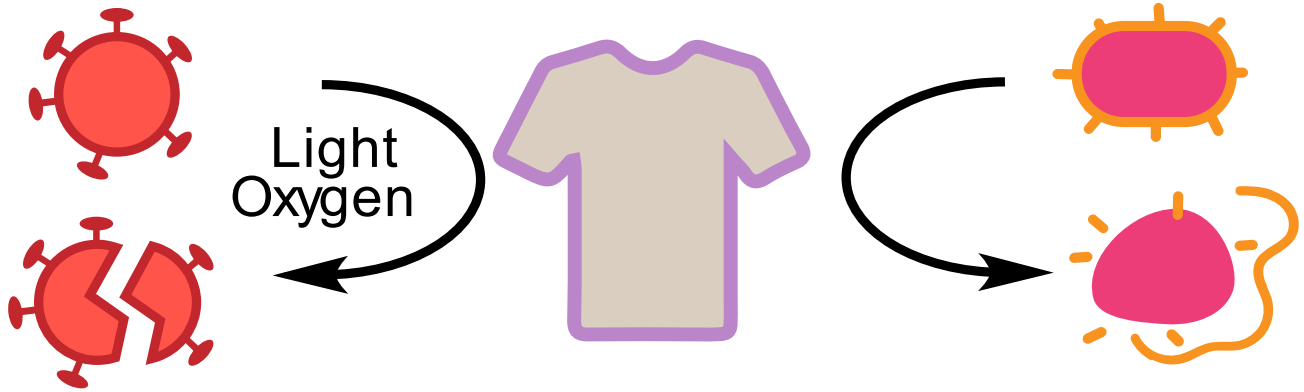




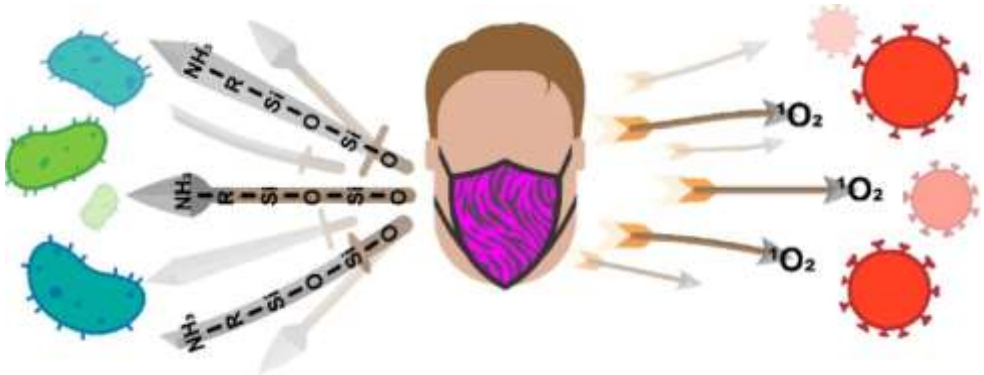
- $^1O_2$ cross-links amines into imines
- Sensitizers can be directly attached to the backbone
- Amines impart antimicrobial activity

Wright, T.; *et al. ACS Appl. Polym. Mater.* **2020**, *2*, 4802–4808.
Wright, T.; *et* al. *ACS Appl. Mater. Interfaces* **2021**, *13*, 22195–22203.

Chapter 6:
Photodynamic and Contact Killing Polymeric Fabric Coating for Bacteria and SARS-CoV-2



CHAPTER 6



- Dual functional polymer coated onto fabrics using $^1O_2$
- High loading with minimal leaching and impact on tensile strength
- Contact killing and aPDI antimicrobial modes for bacteria and SARS-CoV-2 (aPDI)

Wright, T.; Vlok, M.; Shapira, T.; Olmstead, A. D.; Jean, F.; Wolf, M. O. *ACS Appl. Mater. Interfaces* **2022**.