

Supplementary Information

Use of photosensitive molecules in the crosslinking of biopolymers: applications and considerations in biomaterials development

Nicolas Santos,^a Eduardo Fuentes-Lemus ^{*b} and Manuel Ahumada ^{*c,d}

^a Institut Químic de Sarrià, Universitat Ramon Llull, Barcelona 08017, Spain.

^b Department of Biomedical Sciences, Panum Institute, Blegdamsvej 3, University of Copenhagen, Copenhagen, 2200, Denmark.

^c Centro de Nanotecnología Aplicada, Facultad de Ciencias, Ingeniería y Tecnología, Universidad Mayor, Santiago 8580745, Chile.

^d Escuela de Biotecnología, Facultad de Ciencias, Ingeniería y Tecnología, Universidad Mayor, Santiago 8580745, Chile.

Corresponding author's emails: eduardo.lemus@sund.ku.dk; manuel.ahumada@umayor.cl

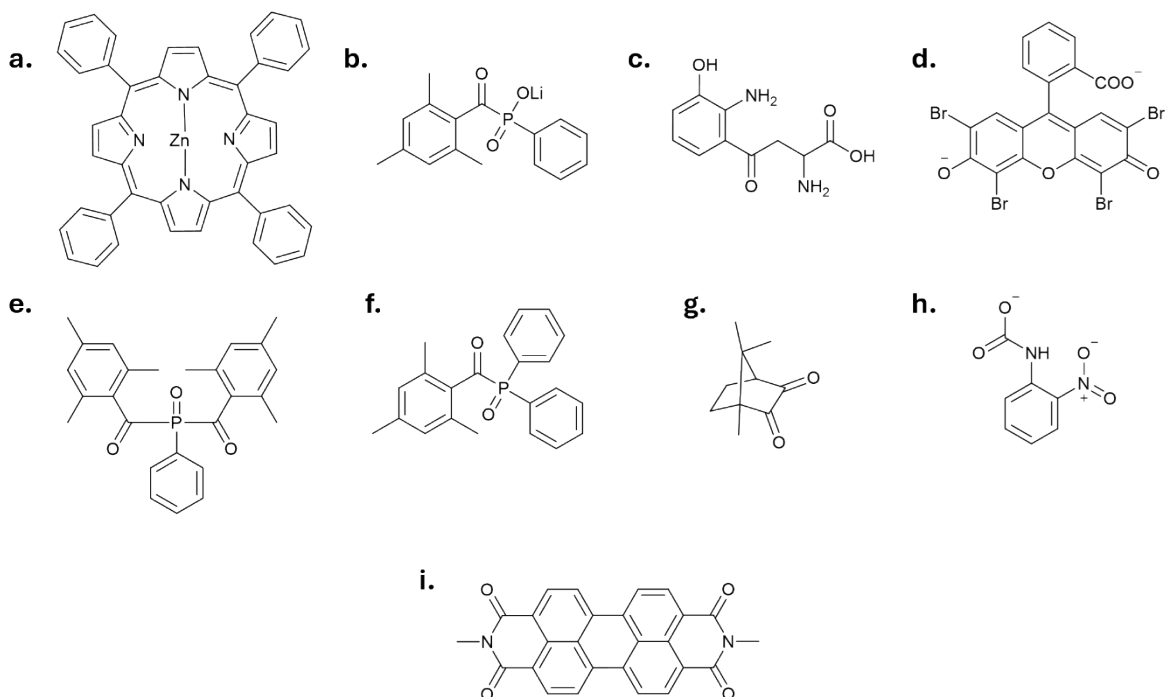


Figure S1. Molecular structure of some of the most employed photosensitizers. a) Zinc(II) meso-tetraphenylporphine; b) Lithium phenyl-2,4,6-trimethylbenzoylphosphinate; c) 3-Hydroxykynurenine; d) Eosin Y; e) phenylbis(acyl) phosphine oxide; f) diphenyl(acyl) phosphine oxide; g) Camphorquinone; h) 2-nitrophenyl carbamate; and i) Perylene diimide.

Table S1. Summary of some biomaterials developed using PSs/Pis and their applications.

Polymer	PSs/PIs	λ_{exc} peak (nm)	Application	Ref
methacrylated collagen	Rose bengal	523	photoactive composite for skin wound closure	1
methacrylated gelatin	bensoylphosphinate derivate	365	Hemostatic and wound heart sealant	2
bovine serum albumin/glycidyl methacrylate	lithium phenyl (2,4,6-trimethyl benzoyl) phosphite	780	Smart biocompatible hydrogel with autofluorescence properties and enhanced chondrocytes proliferation	3
gelatin/glycidyl methacrylate	Irgacure 2959	365	Potential scaffold for liver applications	4
Chitosan/PVA	silicon(IV)phthalocyanine	660	Composite nanofibers with red light-sensitive antibacterial activity	5
Collagen	Riboflavin	360	Promotion of meniscus regeneration and improvement of the mechanical properties	6
Poly(dimethylsiloxane) (PDMS)	Platinum (II) octaethylporphyrin	530	Type II photo-oxidation reaction for the preparation of photopatterned silicone microfluidic devices comparable with the UV-curable siloxanes	7
methacrylated gelatin (GelMA) & methacrylated pectin (PeMA)	Irgacure 2959	365	Hydrogel with antibacterial activity and pH-dependent release of curcumin for the treatment of chronic wounds.	8
Alginate, chondroitin sulfate & Gelatin	2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpro-piophenon	365	3D-hydrogel with a high printability and resolution, enhanced biocompatibility, and bioactivity for tissue engineering	9
Silk fibroin & Gelatin	UiO-66 & methylene blue	460 & 660	3D printable hydrogel with the capability to promote the healing of infected wounds through light-mediated bacterial inactivation	10
Methacrylated alginate (Alg-MA) & Methacrylated heparin (Hep-GM)	Eosin Y & TEOA	525	Hydrogel stimulates tubular network formation for tissue healing in case of thoracic injury	11
PVA	Rose bengal	550	Antibacterial activity by ROS production <i>in vitro</i> and <i>in vivo</i> for wound healing	12
Poly(d,l-lactide) Nanofibers	Curcumin & Indocyanine Green	424 & 797	Antibacterial effect in gram-positive and gram-negative bacteria by the photothermal effect of Indocyanine Green (irradiated at 810 nm) and the release of curcumin to promote the formation of ROS (457 nm irradiation)	13
Cellulose fiber	Toluidine blue	660	Antibacterial activity against <i>E. coli</i> under simulated solar irradiation	14
Acrylic resin	nano-resveratrol	450	Antimicrobial effect against polymicrobial biofilms with an anti-inflammatory response in human gingival fibroblast cells (HGF cells)	15
Chitosan & polyethylene oxide	Sulfonated aluminum phthalocyanine	675	Antibacterial activity against <i>S. aureus</i> in the nanofibers produced by electrospinning	16
PEG-DA-700	Irgacure 819 & 2-isopropyl thioxanthone (ITX)	385	In vitro vascularization of endothelial cells mediated by a stereolithographic printing resin for the development of a 3D-printed chip	17
PEGMA, PEGA & Methyl methacrylate (MMA)	zinc phthalocyanine	730	Photo-induced RAFT polymerization without deoxygenation, high atom economy, and aqueous polymerization	18
Methacrylated carboxymethyl	Lithium phenyl-2,4,6-trimethylbenzoylphos	405	Injectable composite with Hydroxyapatite microspheres for bone tissue regeneration evaluated in rat cranial	19

cellulose	phinate (LAP)		defect	
2-hydroxyethyl methacrylate	Carboxylated-camphorquinone (CQCOOH)	460	Enhance mechanical properties of biocompatible hydrogels	20
Poly(ethylene glycol) Diacrylate	Camphorquinone (CQ)	470	PEGDA hydrogels with multidomain structures DNA-conjugated for controllable release of oligonucleotides	21
polypropylene fumarate	bis-acylphosphine oxide (BAPO)	365	Development of a composite to promote bond regeneration and antibiotic delivery	22
Chitosan/PEGDM A600	benzophenone	253	Design of a biomimetic bone scaffold with various bioceramics to enhance the mechanical properties	23
PmA/MDEA	mono-allyl- and triallyl-purpurin	405	Design of 3D printer biomaterial which promotes the inhibition of bacterial adhesion upon visible-light exposure	24

References

- 1 J. Pupkaite, M. Ahumada, S. Mclaughlin, M. Temkit, S. Alaziz, R. Seymour, M. Ruel, I. Kochevar, M. Griffith, E. J. Suuronen and E. I. Alarcon, *ACS Appl Mater Interfaces*, 2017, **9**, 9265–9270, DOI: 10.1021/acsami.7b01984.
- 2 Y. Hong, F. Zhou, Y. Hua, X. Zhang, C. Ni, D. Pan, Y. Zhang, D. Jiang, L. Yang, Q. Lin, Y. Zou, D. Yu, D. E. Arnot, X. Zou, L. Zhu, S. Zhang and H. Ouyang, *Nat Commun*, 2019, **10**, DOI:10.1038/s41467-019-10004-7.
- 3 T. Li, J. Liu, M. Guo, F. C. Bin, J. Y. Wang, A. Nakayama, W. C. Zhang, F. Jin, X. Z. Dong, K. Fujita and M. L. Zheng, *Int J Bioprint*, 2023, **9**, DOI:10.18063/ijb.752.
- 4 M. M. Sk, P. Das, A. Panwar and L. P. Tan, *Materials Science and Engineering C*, 2021, **123**, DOI: 10.1016/j.msec.2020.111694.
- 5 A. Galstyan and K. Stokov, *Photochemical and Photobiological Sciences*, 2022, **21**, 1387–1398, DOI: 10.1007/s43630-022-00229-9.
- 6 J. Heo, R. H. Koh, W. Shim, H. D. Kim, H. G. Yim and N. S. Hwang, *Drug Deliv Transl Res*, 2016, **6**, 148–158, DOI: 10.1007/s13346-015-0224-4.
- 7 T. Wright, T. Tomkovic, S. G. Hatzikiriakos and M. O. Wolf, *ACS Appl Polym Mater*, 2020, **2**, 4802–4808, DOI: 10.1021/acsapm.0c00778.
- 8 N. S. Bostancı, S. Büyüksungur, N. Hasirci and A. Tezcaner, *Biomaterials Advances*, 2022, **134**, DOI: 10.1016/j.msec.2022.112717.
- 9 F. Olate-Moya, L. Arens, M. Wilhelm, M. A. Mateos-Timoneda, E. Engel and H. Palza, *ACS Appl Mater Interfaces*, 2020, **12**, 4343–4357, DOI: 10.1021/acsami.9b22062.
- 10 Z. Li, A. Zheng, Z. Mao, F. Li, T. Su, L. Cao, W. Wang, Y. Liu and C. Wang, *Int J Bioprint*, 2023, **9**, DOI: 10.18063/ijb.773.
- 11 P. N. Charron, L. M. Garcia, I. Tahir and R. A. Floreani, *J Mech Behav Biomed Mater*, 2022, **125**, DOI: 10.1016/j.jmbbm.2021.104932.
- 12 Y. Li, J. Wang, Y. Yang, J. Shi, H. Zhang, X. Yao, W. Chen and X. Zhang, *Materials Science and Engineering C*, 2021, **118**, DOI: 10.1016/j.msec.2020.111447.

- 13 B. Gutberlet, E. Preis, V. Roschenko and U. Bakowsky, *Pharmaceutics*, 2023, **15**, DOI:10.3390/pharmaceutics15020327.
- 14 D. Langerreiter, K. Solin, M. Jordà-Redondo, R. Bresolí-Obach, L. Fliri, S. Nonell, M. A. Kostianen and E. Anaya-Plaza, *Mater Today Commun*, 2024, **38**, 107858, DOI: 10.1016/j.mtcomm.2023.107858.
- 15 M. Pourhajibagher, R. Bahrami, F. Bazarjani and A. Bahador, *Photodiagnosis Photodyn Ther*, 2023, **43**, DOI: 10.1016/j.pdpdt.2023.103669.
- 16 A. N. Severyukhina, N. V. Petrova, A. M. Yashchenok, D. N. Bratashov, K. Smuda, I. A. Mamonova, N. A. Yurasov, D. M. Puchinyan, R. Georgieva, H. Bäumlér, A. Lapanje and D. A. Gorin, *Materials Science and Engineering C*, 2017, **70**, 311–316, DOI: 10.1016/j.msec.2016.09.005.
- 17 Y. T. Kim, J. S. Choi, E. Choi and H. Shin, *Eur Polym J*, 2021, **151**, DOI: 10.1016/j.eurpolymj.2021.110451.
- 18 S. Zhang, C. Tian, X. Jiang, X. Xu, H. Zhao, J. Sun, L. Zhang and Z. Cheng, *Eur Polym J*, 2023, **196**, DOI: 10.1016/j.eurpolymj.2023.112313.
- 19 H. Qiu, J. Wang, H. Hu, L. Song, Z. Liu, Y. Xu, S. Liu, X. Zhu, H. Wang, C. Bao and H. Lin, *Carbohydr Polym*, 2024, **333**, DOI: 10.1016/j.carbpol.2024.121987.
- 20 E. A. Kamoun, A. Winkel, M. Eisenburger and H. Menzel, *Arabian Journal of Chemistry*, 2016, **9**, 745–754, DOI: 10.1016/j.arabjc.2014.03.008.
- 21 P. J. Dorsey, M. Rubanov, W. Wang and R. Schulman, *ACS Macro Lett*, 2019, **8**, 1133–1140, DOI: 10.1021/acsmacrolett.9b00450.
- 22 I. Qayoom, A. Prasad, E. Srivastava, K. M. Fazili, A. K. Nussler and A. Kumar, *Biomaterials Advances*, 2024, **157**, DOI: 10.1016/j.bioadv.2023.213714.
- 23 F. A. Azaman, K. Zhou, M. del M. Blanes-Martínez, M. Brennan Fournet and D. M. Devine, *Gels*, 2022, **8**, DOI:10.3390/gels8110696.
- 24 P. Sautrot-Ba, V. Brezová, J. P. Malval, A. Chiappone, L. Breloy, S. Abbad-Andaloussi and D. L. Versace, *Polym Chem*, 2021, **12**, 2627–2642, DOI: 10.1039/d1py00126d.