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Synthesis of Zinc Glycoconjugated Phthalocyanines as a Potential Phototherapeutic

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What is PhotoDynamic Therapy (PDT)?

Photodynamic Therapy (PDT) is a non-invasive type of phototherapy

- Utilizes a combination of a photosensitizer (phototherapeutic), light, and molecular oxygen
- A light-activated photosensitizer converts molecular oxygen to a reactive oxygen species (ROS)
- ROS causes oxidative damage and may lead to cell destruction

PHOTODYNAMIC THERAPY

Person with cancer receives a drug called a photosensitizer.

In 24 to 72 hours, cancer cells absorb the photosensitizer.

Cancer cells that absorbed the photosensitizer are exposed to light.

Light causes photosensitizer to make a form of oxygen that kills cancer cells.

Light

Photosensitizer

Activated photosensitizer

Substrate

Reactive oxygen species

Type 1

Type 2

Singlet oxygen

Chem. Soc. Rev. 2011, 40, 340-362; Chem. Soc. Rev. 2016, 45, 6488-6519

Phototherapeutics

Current Medical Applications

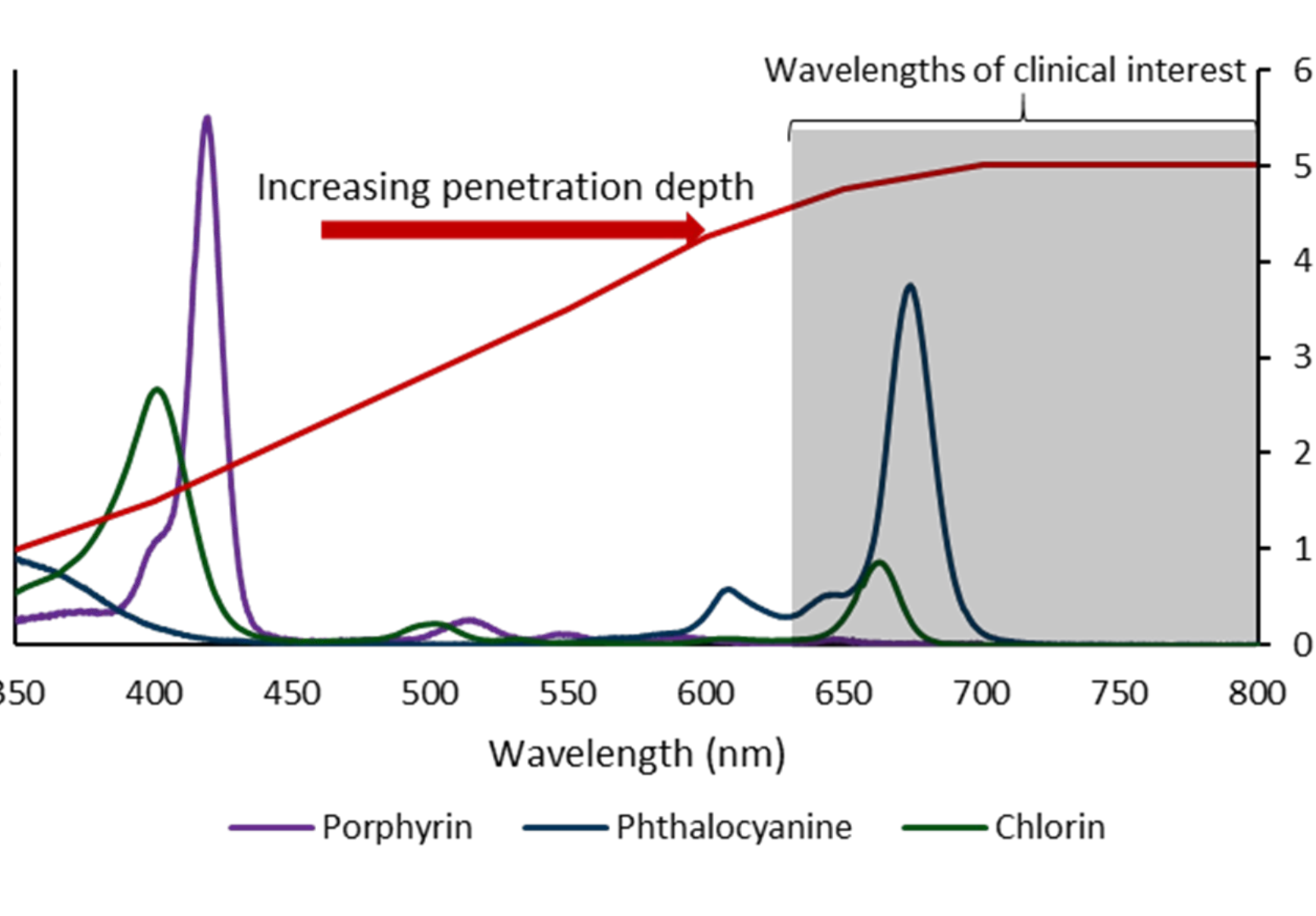
- Skin conditions such as acne and eczema
- Macular degeneration (Visudyne®)
- Variety of solid cancers such as skin, liver, bladder, among others (Photofrin®, Foscan®)

Photodynamic Therapy with Selective Laser Treatment

Image from: PDT induced acute exudative maculopathy | OPTH

Chem. Soc. Rev. 2011, 40, 340-362; Chem. Soc. Rev. 2016, 45, 6488-6519

Photosensitizers for PDT



Development of Phthalocyanines as Phototherapeutics

Challenges (Bioavailability):

- Low solubility in aqueous systems
- Large flat aromatic structure – leads to “stacking”
- Highly non-polar

Potential solution:

- Glycoconjugation
- Increase structural bulk and disrupts “stacking”
- Increase solubility in aqueous systems

Approx. Depth of Penetration (mm)

Chem. Soc. Rev. 2011, 40, 340-362; Chem. Soc. Rev. 2016, 45, 6488-6519

Glycoconjugation via a “Click Reaction”

The Copper-Catalyzed Azide-Alkyne Cycloaddition (CuAAC)

- Often referred to as “click reaction”
- A reliable method used for the linking of carbohydrates
- Previously used in the examination of glycoconjugated porphyrinoids

1. Molecule

2. Molecule

3. Molecule

Click

Chem. Soc. Rev. 2011, 40, 340-362; Chem. Soc. Rev. 2016, 45, 6488-6519

Development of a “Pre-Functionalization” Synthetic Route for Glycoconjugate Phthalocyanines

4-nitrophthalonitrile

Alkynylated Phthalonitrile

Glycoconjugated Phthalonitrile

Chem. Soc. Rev. 2011, 40, 340-362; Chem. Soc. Rev. 2016, 45, 6488-6519

Synthesis of Glycoconjugated Phthalonitriles

4-nitrophthalonitrile

Alkynylated Phthalonitrile

Glycoconjugated Phthalonitrile

Chem. Soc. Rev. 2011, 40, 340-362; Chem. Soc. Rev. 2016, 45, 6488-6519

Synthesis of Glycoconjugated Phthalocyanines

4-nitrophthalonitrile

Alkynylated Phthalonitrile

Glycoconjugated Phthalonitrile

Chem. Soc. Rev. 2011, 40, 340-362; Chem. Soc. Rev. 2016, 45, 6488-6519

Proposed “Post-functionalization” Synthetic Route

4-bromophthalonitrile

Alkynylated Phthalonitrile

Glycoconjugated Phthalonitrile

Chem. Soc. Rev. 2011, 40, 340-362; Chem. Soc. Rev. 2016, 45, 6488-6519

Ongoing Work and Acknowledgements

Solving challenges with purifying A₃B and A₄ for both “pre” and “post” functionalization routes

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