Synthesis of conjugated polymer based in Zn(II) porphyrin bearing terminal alkynyl groups as photosensitizer

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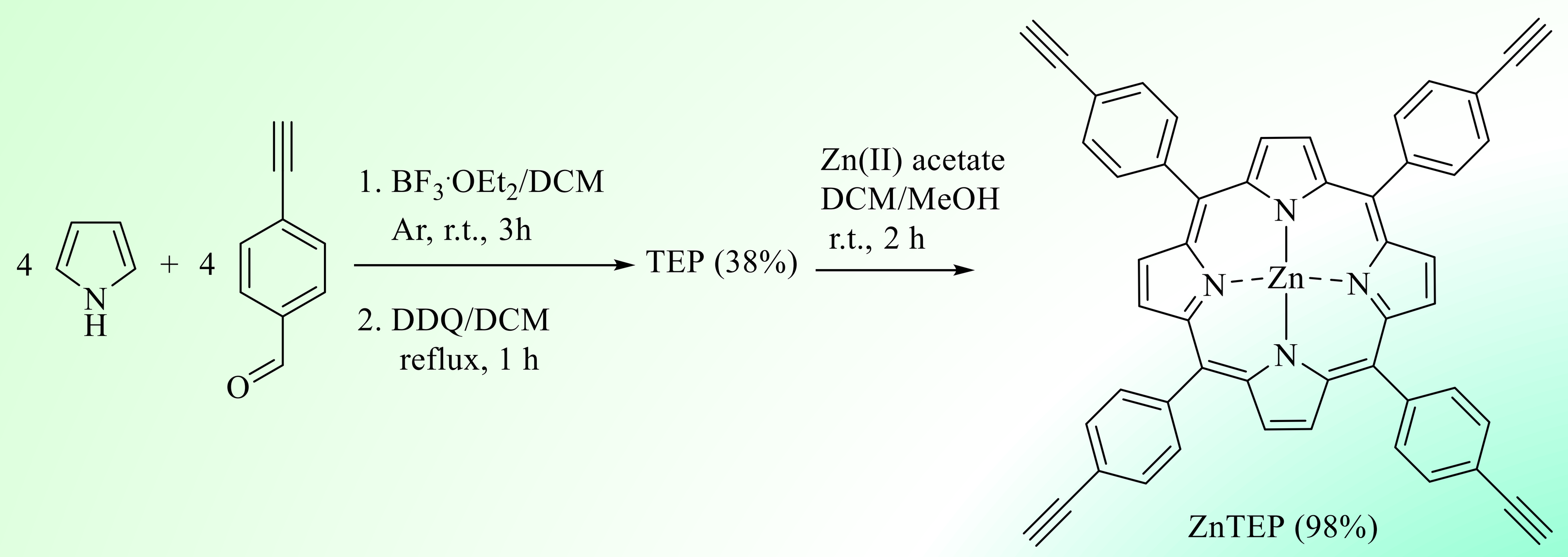
In hospitals, surfaces are one of the main components of possible reservoirs of bacteria, which can cause a notable incidence in nosocomial infections [1]. For this purpose, photodynamic inactivation (PDI) of microorganisms has been proposed to eliminate bacteria. This therapy uses a photosensitizer, visible light and oxygen to produce highly reactive oxygen species (ROS), which can react with several cell components. These molecular modifications induce a loss of biological functionality that causes cell death [2]. In most PDI studies, photosensitizers are added to a microbial suspension from a homogeneous solution. In this methodology, after PDI treatment the photosensitizer remains in the place of action, producing an undesired photodynamic effect and contaminating the medium. In addition, under these conditions the photodynamic agent is difficult to recover for its reuse in subsequent applications. This drawback can be avoided by using photosensitizers chemically bound to a support [3]. Thus, porphyrins immobilized on a surface have been proposed for the inactivation of microorganisms, considering economic and ecological subjects. In this sense, the coating of surfaces with photosensitizers (PSs) that are immobilized in a film are of great interest to maintain aseptic surfaces in public health [4].

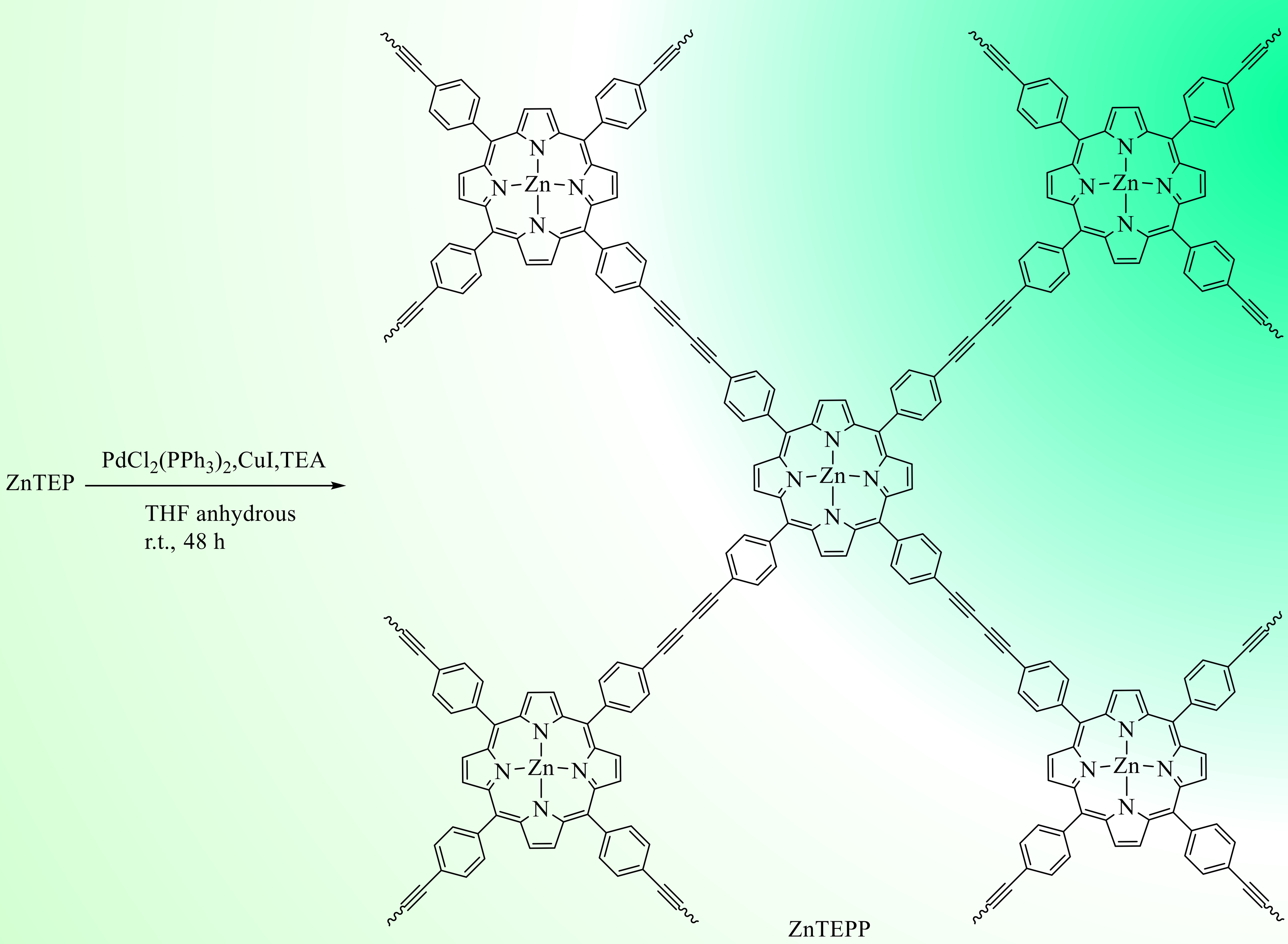
In this study, 5,10,15,20-tetrakis-[4-(ethynyl)phenyl]porphyrin (TEP) was synthesized by acid catalyzed condensation of 4-(ethynyl)benzaldehyde and pyrrole. This porphyrin was treated with Zn(II) to form the complex ZnTEP. Homocoupling reaction of terminal alkynes of ZnTEP to diynes was used to obtain the conjugated polymer organogel (ZnTEPP). After evaporation of the solvent, xerogel was obtained, which is a type of solid-formed gel that has a microporous structure and larger surface area together with very smaller pore sizes. Moreover, spectroscopic and photodynamic studies of ZnTEPP indicated that the porphyrin unit retains its properties as PS. Thus, this polymer is an interesting material with potential applications to form photoactive aseptic surfaces.

Synthesis of porphyrins



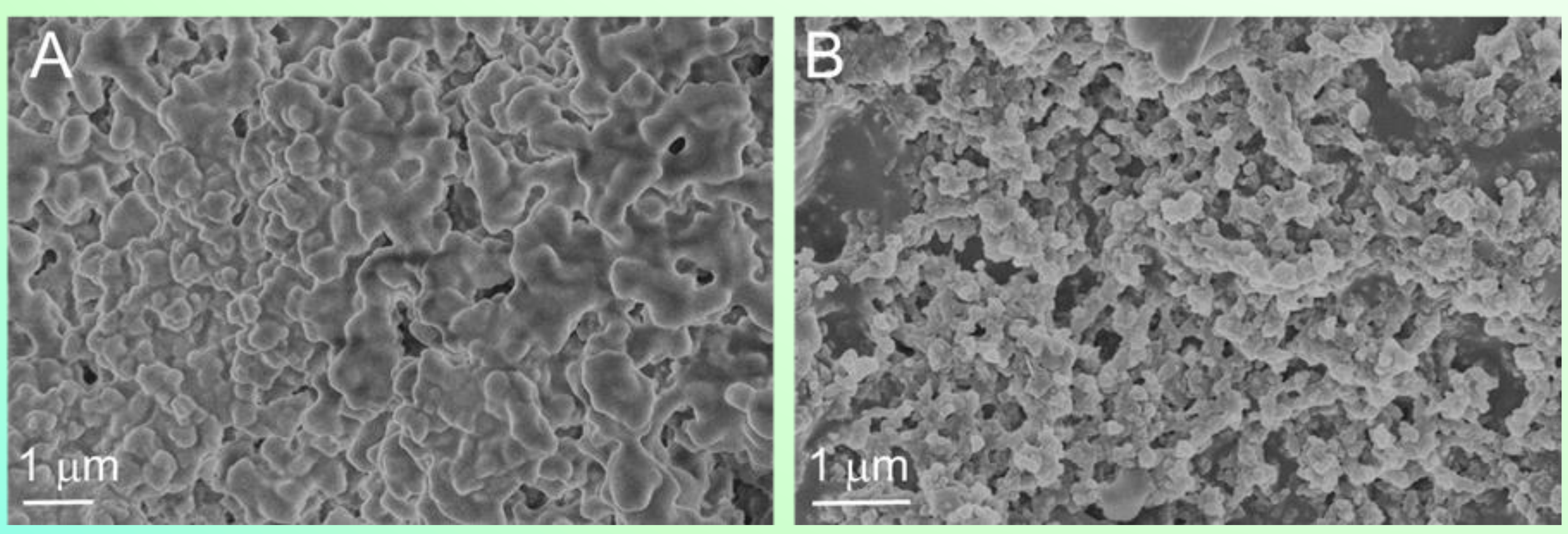
Synthesis of TEP and ZnTEP

Synthesis of polymer



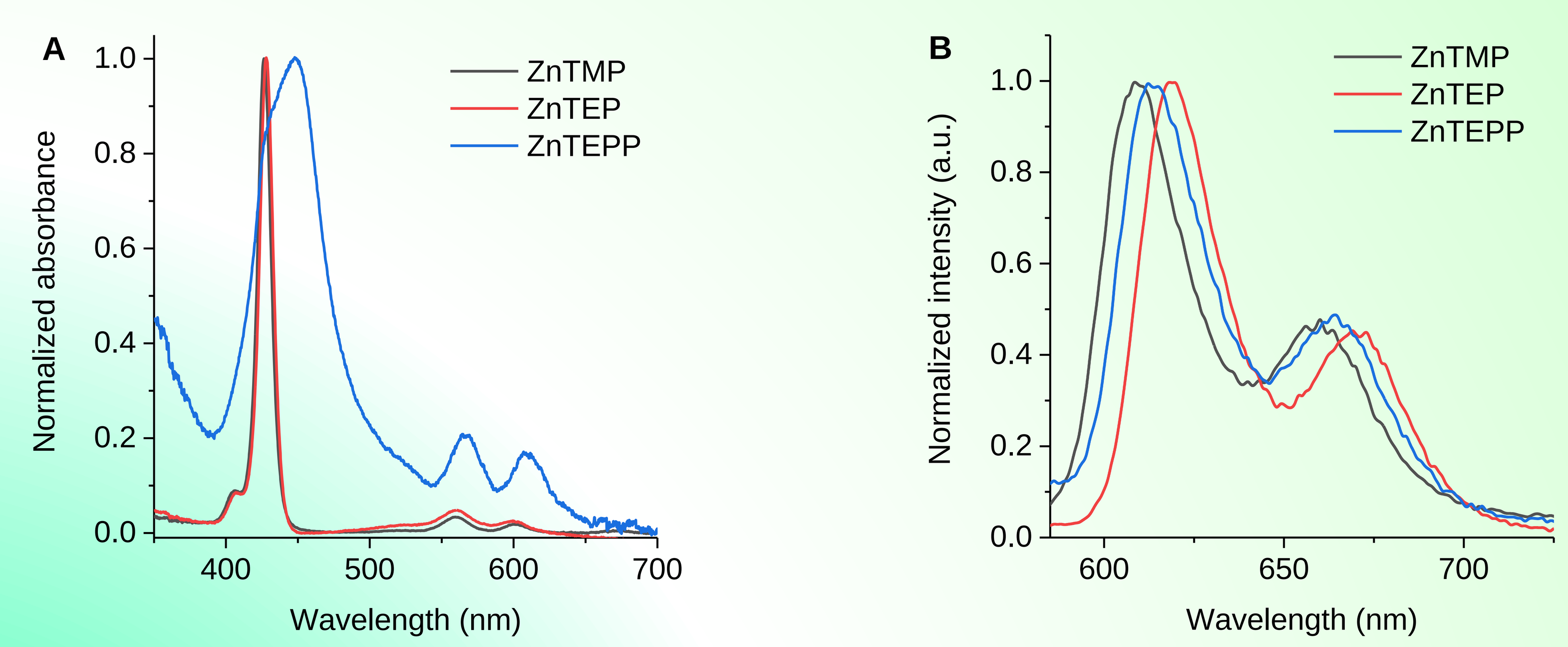
Synthesis of ZnTEPP

SEM images



SEM images of ZnTEPP polymer (A) ZnTEPP organogel deposited as a film on glass and (B) a portion of ZnTEPP xerogel.

Photophysical characterization



(A) UV-visible absorption spectra and (B) fluorescence emission spectra of ZnTMP, ZnTEP and ZnTEPP in DMF, λ_{exc} = 550 nm.

Photodynamic properties

Table 1. Spectroscopic and photodynamic properties of ZnTMP, ZnTEP and ZnTEPP in DMF.

PS	λ^{Soret} (nm)	$\varepsilon^{Soret\ a}$	λ_{em}(nm)	Φ_F [b]	k_{obs}^{DMA} (s^{-1}) [c]	Φ_Δ [d]
ZnTMP	426	$4.07\text{x}10^5$	608	0.049±0.004	(2.02±0.02)x10^{-2}	0.73±0.03 [e]
ZnTEP	428	$5.56\text{x}10^5$	612	0.030±0.003	(1.60±0.02)x10^{-2}	0.57±0.03
ZnTEPP	446	-	620	0.008±0.002	(0.53±0.01)x10^{-4}	0.019±0.004

[a] molar absorption coefficient ($Lmol^{-1}cm^{-1}$), [b] fluorescence quantum yield, [c] observed rate constants for the photooxidation reaction of DMA, [d] quantum yield of $O_2(^1\Delta_g)$ production, [e] from Ref. [5]. Values represent the mean ± standard deviation of three separate experiments.

Conclusiones

The symmetrically meso substituted porphyrin TEP was synthesized from the condensation of 4-(ethynyl)benzaldehyde and pyrrole catalyzed by acid in good yield. This porphyrin was metaled with Zn(II) acetate to form the complex ZnTEP. Homocoupling reaction of terminal alkynes of ZnTEP to diynes was used to synthesize conjugated polymer organogel ZnTEPP. Moreover, the solvent was removed to obtain xerogel. SEM images of ZnTEPP showed microporous structures. The ZnTEPP polymer retains the spectroscopic characteristics of the porphyrin-based chromophore despite to be an extensively polymeric system. In addition, photodynamic studies indicated that the porphyrin unit in ZnTEPP retains its properties as PS, which was able to produce $O_2(^1\Delta_g)$. Thus, this polymer is an interesting material with potential applications to form photoactive aseptic surfaces.

References

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