



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Photophysical studies of newly derivatized mono substituted phthalocyanines grafted onto silica nanoparticles via click chemistry



Adedayo Fashina, Edith Amuhaya, Tebello Nyokong*

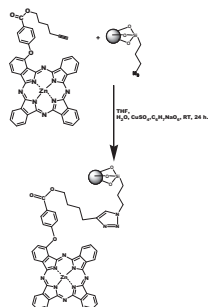
Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

HIGHLIGHTS

- Three phthalocyanines containing terminal alkyne group are synthesized from mono carboxy substituted derivatives.
- The phthalocyanines containing terminal alkyne group showed improved triplet state parameters.
- The phthalocyanines are conjugated to silica nanoparticles via click chemistry.

GRAPHICAL ABSTRACT

The alkyne derived phthalocyanines showed improved photophysical properties compared to the respective phthalocyanine complexes from which they were derived. The derived phthalocyanine complexes were conjugated to the surface of an azide functionalized silica nanoparticles via copper (I) catalyzed cyclo-addition reaction.



ARTICLE INFO

Article history:

Received 12 September 2014

Received in revised form 5 December 2014

Accepted 17 December 2014

Available online 25 December 2014

Keywords:

Phthalocyanine
Silica nanoparticles
Triplet quantum yields
Fluorescence
Lifetimes
Click chemistry

ABSTRACT

This work reports on the synthesis, characterization and photophysical studies of newly derived phthalocyanine complexes and the phthalocyanine–silica nanoparticles conjugates. The derived phthalocyanine complexes have one terminal alkyne group. The derived phthalocyanine complexes showed improved photophysical properties (Φ_F , Φ_T , Φ_A and τ_T) compared to the respective phthalocyanine complexes from which they were derived. The derived phthalocyanine complexes were conjugated to the surface of an azide functionalized silica nanoparticles via copper (I) catalyzed cyclo-addition reaction. All the conjugates showed lower triplet quantum yields ranging from 0.37 to 0.44 compared to the free phthalocyanine complexes. The triplet lifetimes ranged from 352 to 484 μ s for the conjugates and from 341 to 366 μ s for the free phthalocyanine complexes.

© 2014 Elsevier B.V. All rights reserved.

Introduction

The ease of functionalizing nanoparticles (such as silica nanoparticles, SiNPs) with different materials such as fluorophores,

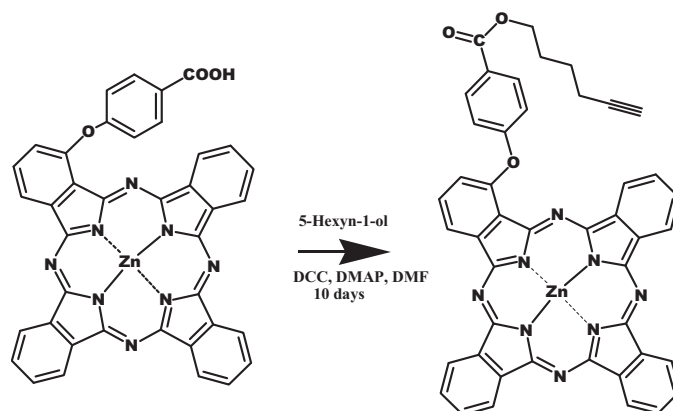
drugs, bio-molecules, dendrimers and polymers, has led to the development of improved and multifunctional materials that have found applications in areas such as drug delivery, sensing, diagnosis, imaging and theranostics [1–7]. Functional groups such as amine, carboxylic acid, thiol, azide and alkyne have been used to functionalize the surface of SiNPs for covalent grafting of materials [8–11]. Click chemistry as proposed by Sharpless and co-workers

* Corresponding author. Tel.: +27 46 6038260; fax: +27 46 6225109.

E-mail address: t.nyokong@ru.ac.za (T. Nyokong).

has continued to generate interest due to its simplicity, selectivity and biocompatibility [12]. A classic click chemistry reaction is the copper (I) catalyzed 1,3-dipolar cyclo-addition between azides and acetylenes. Click chemistry has been used to functionalize fluorophores such as phthalocyanines (Pcs) [13–15]. However, not much has been done on the grafting of phthalocyanine complexes to the surface of silica nanoparticles via click chemistry though in previous studies we have grafted Pcs to the SiNPs via amide and ester bonds [16,17].

In this work, we report on the synthesis and characterization of three new mono substituted zinc phthalocyanine complexes (**1a**, **2a** and **3a**) each having a terminal alkyne group (at the peripheral or non peripheral positions), Fig. 1. Complexes **1a** and **2a** contain the same substituent derived from 3-carboxyphenoxy, but **2a** is peripherally substituted while **1a** is non-peripherally substituted. **1a** and **3a** are both non-peripherally substituted, but the former is derived from the 3-carboxyphenoxy while the latter from 4-carboxyphenoxy. Asymmetrical phthalocyanines are challenging to synthesize due to the formation of a variety of derivatives. The new phthalocyanine complexes were derived (Scheme 1, using **3a** as a representative) from previously reported complexes (**1**, **2** and **3**) [18]. The three new complexes (**1a**, **2a** and **3a**) were further grafted to the surface of azide functionalized SiNPs via click chemistry, (Scheme 2). The hybrid nanocomposites formed are represented as **1a**-SiNPs, **2a**-SiNPs and **3a**-SiNPs. The photophysical properties of the new complexes (**1a**, **2a** and **3a**) are compared to those of the hybrid particles (**1a**-SiNPs, **2a**-SiNPs and **3a**-SiNPs).



Scheme 1. Synthetic route for the formation of complex **3a** (representative of **1a** and **2a**).

We also carried out studies where the azide functionalized SiNPs were mixed with the Pc complexes (without formation of a chemical bond) and these complexes are represented as **1a**-SiNPs (mixed) **2a**-SiNPs (mixed) and **3a**-SiNPs (mixed). The mixed complexes were studied to evaluate the effect of the SiNPs on the photophysical properties of the Pcs in the absence of a covalent bond.

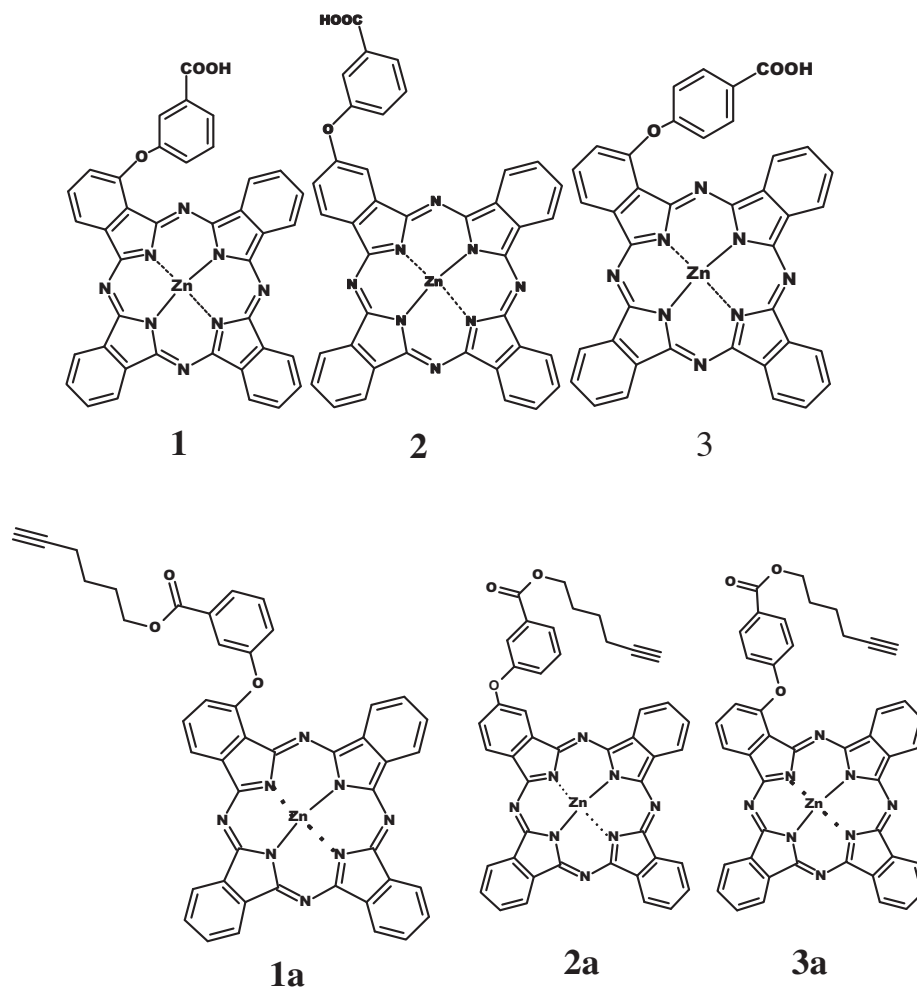


Fig. 1. Chemical structures for complexes **1**, **2** and **3** and the corresponding **1a**, **2a**, and **3a**.

Download English Version:

<https://daneshyari.com/en/article/1229378>

Download Persian Version:

<https://daneshyari.com/article/1229378>

[Daneshyari.com](https://daneshyari.com)