Journal of Luminescence 195 (2018) 348–355

Contents lists available at ScienceDirect

Journal of Luminescence

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

Gold nanoparticles-pyrrolidinonyl metal phthalocyanine nanoconjugates: Synthesis and photophysical properties

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ARTICLE INFO

Keywords:
Pyrrolidinonyl
Phthalocyanine
Gold nanoparticles
Photophysical property
Nanoconjugate
Fluorescence quantum yield

ABSTRACT

A novel series of pyrrolidinonyl metal phthalocyanines (PyMPc, M = Zn, Cu, Co and Ni) was synthesized. Their structures were characterized by IR, ^{1}H NMR, ESI-MS as well as elemental analysis. The photophysical properties of PyMPcs were studied by UV/vis and fluorescence spectroscopic methods. AuNPs-MPEG-PyMPc nanoconjugates were prepared by conjugating the thiolatedmethoxypolyethylene glycol capped gold nanoparticles (AuNPs-MPEG) with PyMPc through a donor-acceptor interaction. UV/Vis spectra and TEM images evidenced that the PyMPcs were conjugated with gold nanoparticles. The photophysical properties of both free PyMPcs and AuNPs-MPEG-PyMPc nanoconjugates exhibited central ions dependence. PyZnPc and AuNPs-MPEG-PyZnPc exhibited the highest fluorescence quantum yields. But the fluorescence lifetimes of AuNPs-MPEG-PyMPc (M = Cu, Co and Ni) were longer than that of corresponding free phthalocyanines.

1. Introduction

Phthalocyanines (Pcs), an 18 π-electron macrocyclic conjugated system, attracted great interest due to their diverse applications in medicinal and materials chemistry [1]. Varying the peripheral/axial substituents and/or the central metals of Pcs, the physical properties could be modulated according to the desired applications [2,3]. For example, introducing some functional bioactive groups, such as alkynyl, morpholinyl, thienyl, or adamantyl groups to the axial/peripheral positions of the phthalocyanine ring, the solubility of phthalocyanines in organic solvents could be enhanced, and the aggregation behaviors could be reduced [4,5]. Pyrrolidone (PVP), a bulky, nontoxic, non-ionic polymer with C=O, C–N and CH_2 functional groups [6,7], not only involved in human metabolism, but also had good biocompatibility with human tissue. It also didn't exert any stimulation to the skin, mucous membrane and eyes [8]. Besides, pyrrolidinonyl ring with a nitrogen heterocyclic structure has been reported as a probe for targeting lysosome [9].

Nanoparticles, such as polymeric nanoparticles, silica nanoparticles and metal nanoparticles, have been widely used as multi-functional drug carriers because their surfaces can be modified with different functional groups [10]. Gold nanoparticles (AuNPs) is regarded as an ideal drug carriers, which have been widely applied in imaging, sensing, medicine, photonics and optics, plasmonic photothermal therapy (PTT) as well as in preclinical and clinical anti-arthritic, anti-cancer, anti-microbial, antiparasitic and anti-HIV studies [11–13]. The surface plasmon resonance (SPR) absorption band of AuNPs with diameters in the range of 2–100 nm is found at about 520 nm [14]. AuNPs can be linked with some recognition moieties, such as antibodies or oligonucleotides for detection of target biomolecules [15–17], or for delivery drug [18–22]. Conjugated AuNPs with phthalocyanines could improve the phthalocyanine's drug delivery efficiencies, modulate its photophysical properties and enhance the singlet oxygen production quantum [23,24]. AuNPs could conjugate with phthalocyanine through Au-S bonds [25–27], N-Au bonds [28], or electrostatic interaction [29–32]. Masilela et al. reported a SH and SR substituted phthalocyanine-AuNP nanoconjugates. It has been found to exhibit a great improvement in the triplet lifetime and a decrease in fluorescence quantum yield and lifetimes for this nanoconjugate when compared to the free phthalocyanine [33]. Cook and coworkers prepared a thiol substituted zinc phthalocyanine-gold nanoparticle, which exhibited excellent photodynamic therapy efficacy against tumour cells [34].

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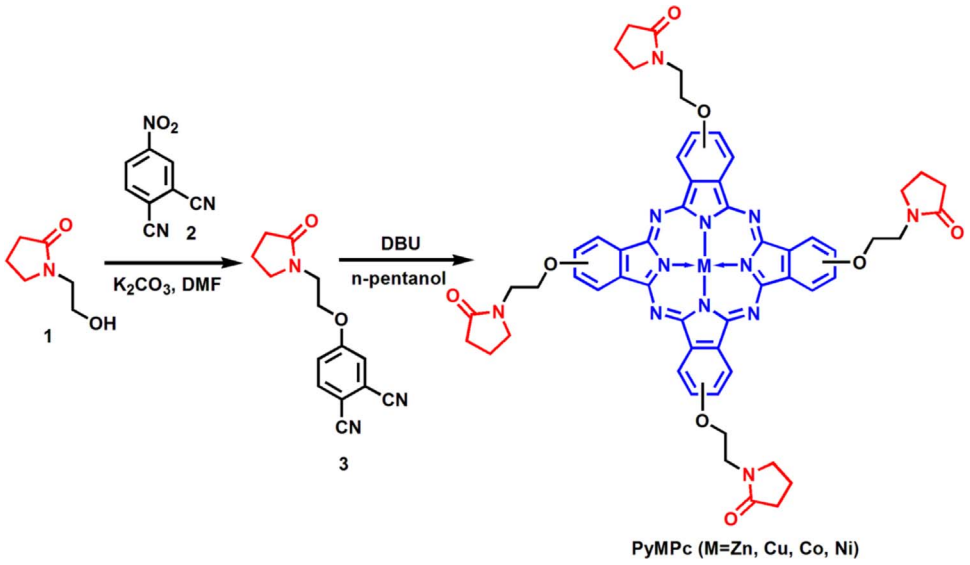
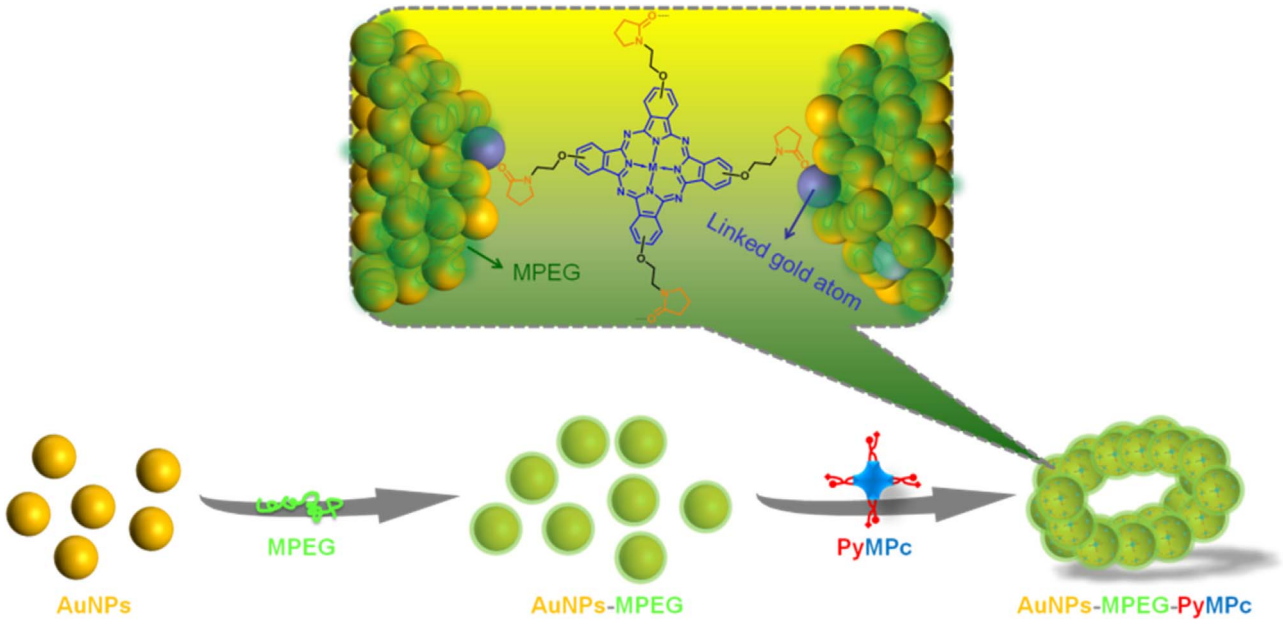
https://doi.org/10.1016/j.jlumin.2017.11.047
Received 23 September 2017; Received in revised form 8 November 2017; Accepted 22 November 2017
Available online 24 November 2017
0022-2313/

Scheme 1. The synthetic route for PyMPc (M = Zn, Cu, Co and Ni).





Scheme 2. The possible formation mechanism of AuNPs-MPEG-PyMPc.

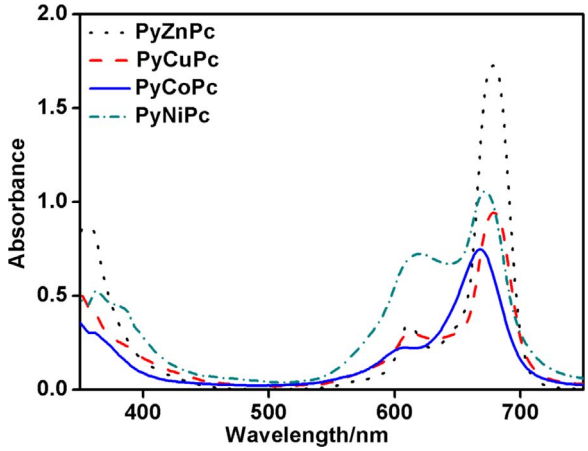


Fig. 1. UV/Vis spectra of PyMPc in DMF (C_{PyMPc} = 1×10^{-5} mol/L).

In this paper a novel series of tetra-(2-pyrrolidinonyl-N-ethyloxy) substituted metal phthalocyanines (PyMPc, M = Zn, Cu, Co and Ni) has been synthesized. Their structures were characterized by elemental analysis, ^{1}H NMR, IR and ESI-MS. Nanoconjugates (AuNPs-MPEG-PyMPc, M = Zn, Cu, Co and Ni) were prepared by conjugating thiolatedmethoxypolyethylene glycol (MPEG-SH) capped gold nanoparticles (AuNPs-MPEG) with PyMPc through a donor-acceptor type interaction [35,36]. The effect of central metal ions on the photophysical properties of both free PyMPcs and nanoconjugates was studied.

2. Experimental

2.1. Materials

All reagents for the synthesis were analytical grade and used as received. Chloroform ($CHCl_3$), dimethylformamide (DMF), dichloromethane (DCM), methanol (MeOH), n-hexane, n-Pentanol, sodium citrate and 1,8-diazabicyclo-(5,4,0)-undec-7-ene (DBU) were purchased from Sinopharm, China. Tetrachloroauric acid ($HAuCl_4$),