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Facile fabrication of white-emitting hybrid colloids and nanocomposite films using CdSe/CdS quantum dots and zinc phthalocyanines as building blocks

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ABSTRACT

In this work, we have designed a facile protocol to prepare white emitting colloid solutions and polymer nanocomposite films via the self-assembly of zinc phthalocyanine (ZnPc) in the presence of semiconductor CdSe/CdS quantum dots (QD). Specifically, a dendritic zinc phthalocyanine showing two independent emission bands at blue (~450 nm) and red region (~690 nm) in N, N-dimethylformamide (DMF) solution was synthesized by using a biphenyl phthalonitrile based precursor. In order to fulfill the missing green emission band and overcome the strong intermolecular aggregation tendency of ZnPc that normally results to obviously quenched fluorescence in solution, an ultrasmall sized CdSe/CdS QD with green emitting capabilities, was synthesized, surface modified with a hydrophobic capping agent (oleic acid) and dispersed uniformly in nonpolar hexane. When the hexane solution of QD was introduced to the immiscible ZnPc solution in DMF, nanoconjugates exhibiting three independent emission bands can be formulated by using ZnPc and QD as building blocks via the non-covalent hydrophobic interaction established in the incompatible DMF/hexane interface. Furthermore, the white emitting ZnPc/QD colloid solutions and nanocomposite films can be readily obtained by controlling the relative concentration of ZnPc and QD.

1. Introduction

Fluorescent materials, especially fluorophores with a multi-emission ability, have attracted increasing research interest recently, mainly due to their potential application in full color display [1], high throughput biochemical sensing/imaging, etc [2,3]. Basically, fluorescent materials can be divided into two major categories consisting of inorganic and organic fluorophores. Apart from the conventional fluorescent materials such as rare earth compounds and small organic dye molecules, a variety of novel fluorescent materials have been developed. For instance, semiconductor quantum dots (QDs) [4,5] and noble metal (gold, silver) [6,7] nanoclusters are representative of high quality ultrasmall nanostructured fluorophores, while some intrinsically fluorescent polymers (such as metallophthalocyanine (MPc) [8], poly(phenylene ethynylene) (PPE) [9] poly(2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV) [10], polyarylene ether nitrile [11]) and fluorescent proteins [12] are newly developed organic fluorophores. Phthalocyanines (Pc) have long been used as dyes and pigments in the textile industry due to their intrinsic blue-green color. It should be noted that increasing research works are using Pc as the building blocks for constructing various advanced optical materials in recent decades. Specifically, the unique two-dimensional conjugated structure and highly delocalized π electrons of Pc are responsible for their versatile optical properties (fluorescence, nonlinear optics, catalysis, photosensitizing ability, etc.), leading to their widespread applications as fluorescent probes [13], nonlinear optical limiting materials [14], photocatalyst [15] and photosensitizer for organic solar cells [16] as well as photodynamic therapy (PDT) [17]. Meanwhile, phthalocyanines have good reactivity, as more than 70 different kinds of transition metals can be coordinated into the Pc rings to form various

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metallophthalocyanine (MPc). Especially, zinc phthalocyanine (ZnPc) is one typical MPc showing dual functionalities of fluorescence and photosensitizing ability due to the closed shell electron structures of central zinc ion [18]. In terms of fluorescence, a representative red or near infrared emission with small Stokes shift was recorded from ZnPc solution in the majority of published work [19–21]. Moreover, the optical properties of ZnPc are highly dependent on their dispersion state in solvent, since the strong intermolecular aggregation tendency of ZnPc would result in the drastic decay of their optical performance. With this in mind, it is envisaged that the photoactive ZnPc superstructures can only be prepared by fine controlling of its self-assembling process in solution. Meanwhile, the ZnPc is virtually non-fluorescent in the wavelength range from 500 nm to 600 nm, which will hinder its practical application as multi-emission fluorophores or wide-band photosensitizer.

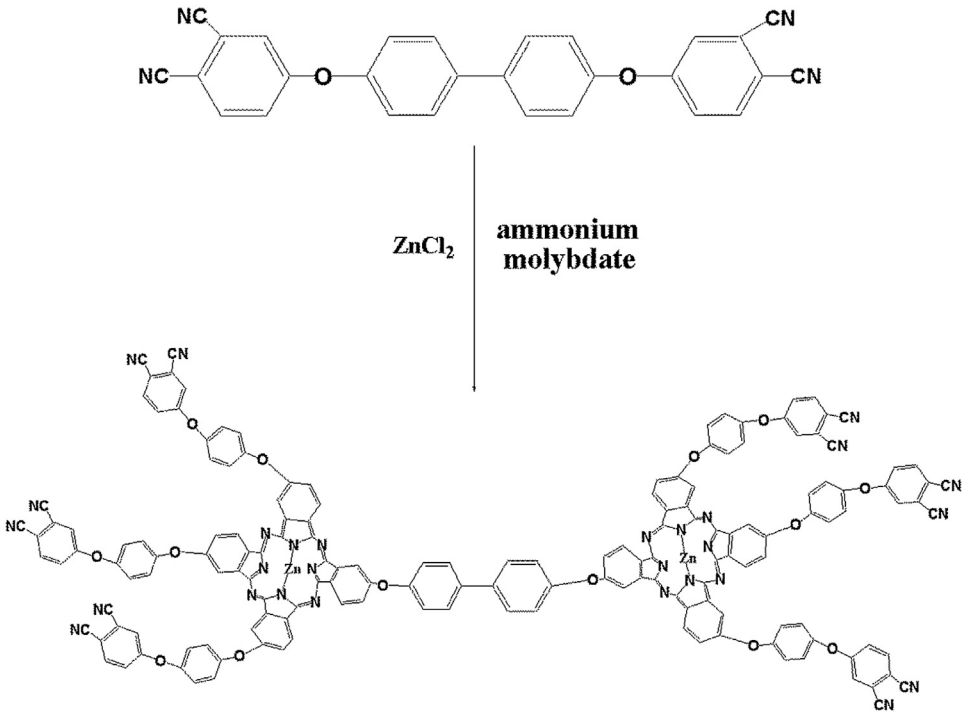
Fortunately, the fluorescent emission wavelength of ultra-small sized semiconductor nanocrystals, also known as quantum dots (QD), can be readily turned in the visible light frequency, especially for the wavelength range of 500–600 nm [22]. Generally, the emission wavelength of QDs is highly dependent on the nanocrystal sizes, shape and composition that can be modified by the reaction conditions (temperature, time, feed ratio of precursors, etc.) [23]. Meanwhile, the QD fluorescence emission with a small full width at half maximum (FWHM) can be excited in large wavelength range, and the QD normally exhibits excellent photostability and high quantum yields (up to 80%) [24]. Thanks to these inherent advantages, QDs can be conjugated with zinc phthalocyanines for preparation as multi-emissive materials. Actually, a variety of different ZnPc/QD nano-conjugates have been designed for biological therapy [25,26] and organic solar cells application [27,28]. For instance, ZnPc and QD can be covalently conjugated together via the well-known protocol based on 1-ethyl-3-(3-dimethylamino) propyl carbodiimide (EDC) and *N*-hydroxy succinimide (NHS) [20,29] or various thiolated ligands [30,31]. Moreover, the ZnPc-QD nanohybrids can be prepared via the non-covalent interaction such as electrostatic adsorption [32]. Although the obtained ZnPc/QD nanoparticles exhibit fluorescent emission bands, the tedious experiment work, complicated chemical synthesis as well as instability of nanoconjugates obtained from non-covalent protocols take place in these published works. On the other hand, the fluorescence emission of ZnPc can be easily quenched in the presence of QDs, which results from the aggregation of the Pc or photo-induced energy transfer [33]. Therefore, it is still challenge to develop a simple and effective protocol to fabricate ZnPc/QD nanoparticles with desired optical properties.

In this work, the ZnPc/QD nano-assemblies, showing three independent emission wavelengths at blue, green and red bands in an organic solution when excited with UV light (365 nm), were synthesized via a solvent interface mediated self-assembling process and subsequently transferred into a transparent poly (methyl methacrylate) (PMMA) film. Since oleic acid capped QDs were incorporated into ZnPc self-assembled superstructures via non-covalent hydrophobic interactions leading to a stable homogeneous colloid solution without any noticeable aggregates, the photophysical spectra of ZnPc/QD nano-assembles remained unchanged for at least one month when stored at 4 °C. Finally, the overall emission spectra of ZnPc/QD nano-assemblies can be readily tuned by simply changing their relative doping concentration, leading to the white-light emitting colloid solutions and flexible polymer films under optimized conditions.

2. Experimental

2.1. Synthesis of zinc phthalocyanine (ZnPc)

The synthesis route and chemical structure of zinc phthalocyanine were shown in Scheme 1. In a typical synthesis, 4, 4′-bis (3,4-dicyanophenoxy) biphenyl (BPH) (0.438 g, 1 mmol), zinc chloride (0.034 g, 0.25 mmol) and ammonium molybdate (5 mg, 4 μmol) were added into 40 mL dimethylacetamide (DMAc) solvent in a three-necked flask. The reaction mixture was heated as solution color turned from light yellow to green, after refluxing



Scheme 1. The synthesis route and chemical structure of zinc phthalocyanine.