



Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Organic nanoparticles of an extended π -conjugated styryl dye: Modulation of fluorescence peak energy and intensity in the near-infrared (NIR) region



Hiroshi Yao*, Tomohito Funada

Graduate School of Material Science, University of Hyogo, 3-2-1 Koto, Kamigori-cho, Ako-gun, Hyogo 678-1297, Japan

ARTICLE INFO

Article history:

Received 23 June 2016

Received in revised form 29 July 2016

Accepted 3 August 2016

Available online 8 August 2016

Keywords:

Styryl dye

Organic nanoparticle

Near-infrared (NIR) fluorescence

Ion association

Co-doping

ABSTRACT

Tuning the near-infrared (NIR) emission of organic nanomaterials is of great interest due to possible use in biosensing and imaging based on the biological window ranged in 650–900 nm. In this study, we report NIR fluorescent organic nanoparticles prepared on the basis of ion association between an extended π -conjugated Styryl-9 cation and tetrakis(4-fluorophenyl)borate (TFPB) anion. Binding of Styryl-9 with TFPB results in the prominent appearance of an absorption band that can be assigned to a non-fluorescent H-aggregate, which is revealed by simultaneous deconvolution of both UV–vis absorption and fluorescence excitation spectra, and supported by quantum chemical calculations. Emission is observed in the NIR region from the nanoparticles, but is reduced by the presence of the H-aggregates. To mitigate the H-aggregation occurred inside the nanoparticle, photochemically-inert, bulky tetraphenylphosphonium cation (co-cation) is concurrently incorporated (co-doped), resulting in the disappearance of the relevant H-aggregates and thereby yielding controllable fluorescence peak energy and intensity in the NIR region. We believe that such methodology for synthesizing ion-based organic nanoparticles with tunable emission will open an avenue in the development of new types of NIR fluorescent nanomaterials.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Among the near-infrared (NIR) organic/inorganic materials, NIR-absorbing materials are diverse and extensive in many technological sectors; for example, digital copy machines as the charge-generation material [1], heat absorbers or optical filters to block the heat [2], and photosensitizers for photodynamic therapy in the treatment of cancer [3]. On the other hand, NIR-emissive materials are relatively less available than the absorbing materials, but they can particularly offer some advantages in biological or cell imaging because of no or low autofluorescence from tissue and deeper penetration of light into the tissues at wavelengths between 650 and 900 nm [4,5]. Such NIR energy region is called “biological window” [6], and there is potential for the development of a noninvasive clinical diagnostic [7,8]. Accordingly, the development of NIR fluorophores for such applications has been receiving strong attention [9–11]. A number of NIR-emissive materials, particularly nanomaterials, have been then exploited,

which include quantum dots [12], fluorescent proteins [13], and polymer dots [14]. In recent years, organic nanoparticles based on small molecules have also attracted much attention since they have additional advantages such as easy synthesis and purification, better biodegradability and chemical tailorability [15,16]. In this regard, organic nanoparticles having favorable NIR photophysical properties such as high quantum yield and thermal/chemical stability are anticipated.

Styryl dyes have been among the most widely used probes for mapping membrane potential changes in excitable cells [17]. In particular, they are generally endowed with large Stokes shifts that make them particularly convenient for microscopy. Another interesting feature is their potentiometric properties so it can probe sensitivity or penetrability of lipids, membranes, and tissues [17]. In the present study, we synthesize organic nanoparticles using an extended π -conjugated styryl dye, Styryl-9, which exhibits NIR emission. Styryl-9 shows quite unique properties, for example, its absorption maximum is sensitive to the medium polarity, whereas its fluorescence energy stays practically constant [18–20]. It also has high two-photon absorption cross sections, that is, fluorescence and excitation wavelengths can be all located in NIR region, so the penetration depth in tissue is maximized, and

* Corresponding author.

E-mail address: yao@sci.u-hyogo.ac.jp (H. Yao).

absorption or photo-damage is minimized [21]. The excited-state relaxation dynamics of this dye has been also investigated in different kinds of solvents using transient spectroscopic techniques, and the presence of at least two kinds of emission states has been revealed [20]; one is the locally-excited (LE) state that is detectable at 700–750 nm, and the other the twisted intramolecular charge-transfer (TICT) state that can be formed by a barrier crossing process to a lower-energy state via the torsional motion in the dye molecule.

The organic nanoparticles of Styryl-9 are synthesized on the basis of the formation of water-insoluble ion-pair solids in aqueous phases by association of a chromophoric Styryl-9 cation with a hydrophobic (non-chromophoric) tetrakis(4-fluorophenyl)borate counteranion [22,23]. The electrostatic interaction and subsequent immobilization of the dye in the solid-state nanoparticle can bring about restriction of its torsional motion, so the control of LE and TICT emission in the NIR region can be expected. Upon the nanoparticle synthesis, non-fluorescent H-aggregates of Styryl-9 molecules are significantly produced, which is confirmed by simultaneous deconvolution analysis of both absorption and fluorescence excitation spectra. Then to mitigate the H-aggregation and related aggregation-caused quenching (ACQ), foreign photochemically-inert tetraphenylphosphonium cations are co-doped (or incorporated) in the nanoparticles. The LE and TICT emissions are controlled by not only the feed stoichiometry between the Styryl-9 cation and borate counteranion but also that between two types of cations, suggesting that rotational free space or rigidity of Styryl-9 molecules can be also modulated in the nanoparticle.

2. Experimental section

2.1. Materials

Styryl-9 perchlorate (laser dye grade (98%); known also as LDS-821 or Styryl-9M) was purchased from Sigma-Aldrich and used as received. Poly(vinylpyrrolidone) (PVP; average $M_w = 10,000$, Aldrich) was used as a neutral stabilizer to prevent particle agglomeration. Sodium tetrakis(4-fluorophenyl)borate dihydrate ($\text{NaTFPB} \cdot 2\text{H}_2\text{O}$, Sigma-Aldrich) and tetraphenylphosphonium chloride (abbreviated as TPPhosCl, Sigma-Aldrich) were of the highest commercial grade available and used as received without further purification.

2.2. Synthesis of organic Styryl-9 nanoparticles

Organic Styryl-9 nanoparticles were prepared by means of the *ion-association* method [22,23]. Typically, at room temperature, rapid addition of aqueous PVP solution (3.0 mL) into the small amount of acetonitrile containing both TFPB (2.0 mM; 15–30 μL) and Styryl-9 (0.5 mM; 60–40 μL) under ultrasonication, at the molar ratio ($\rho = [\text{TFPB}]/[\text{Styryl-9}]$) changing from 1 to 3, produced almost clear purple suspension. The concentration of PVP was set at 0.4 mg/mL, giving no particle flocculation and thus spectroscopic reproducibility for the samples. The consequent Tyndall scattering gave confirmatory evidence that ion-association between cationic Styryl-9⁺ and anionic TFPB⁻ led to the formation of water-insoluble Styryl-9 nanoparticles.

2.3. Co-doping of photochemically-inert phosphonium cation inside the Styryl-9 nanoparticles

We find that formation of non-fluorescent H-aggregates of Styryl-9 is significant in the organic nanoparticles. Hence to mitigate the formation of H-aggregates, we tried dilution of the Styryl-9 concentration inside the solid-state organic nanoparticles

by mixing (or co-doping) the photochemically-inert hydrophobic tetraphenylphosphonium (TPPhos) cations [24]. In other words, the purpose of inclusion of TPPhos inside the Styryl-9 nanoparticles is to actively control spectroscopic (absorption and fluorescence) properties of the dye nanoparticles.

The TPPhos-incorporated Styryl-9 nanoparticles were prepared by the ion-association protocol between the binary mixture of cationic Styryl-9 and TPPhos, and anionic TFPB under the condition of $\rho = 1$ or 3 (in this case, $\rho = [\text{TFPB}]/([\text{Styryl-9}] + [\text{TPPhos}])$), in the presence of PVP ([PVP] = 0.4 mg/mL). The mixing ratio (molar fraction) of TPPhos to Styryl-9 ($[\text{TPPhos}]/[\text{Styryl-9}]$) was changed from 3 to 5.

2.4. Instrumentation and computation

Morphology and size of the nanoparticles were examined with a Hitachi S-4800 scanning transmission electron microscope (STEM). A specimen for STEM observations was prepared by dropping the suspension on an amorphous carbon-coated copper mesh. UV–vis absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Fluorescence spectra were obtained with a Hitachi F-4500 spectrofluorometer. Fluorescence quantum yields (Φ_f) were approximately determined by comparing the emission spectra of Styryl-9 in chloroform ($\Phi_f = 0.1$) [20].

In computational methods, ground-state geometry calculations were carried out with the Gaussian 09 program at the density functional theory (DFT) level using B3LYP functional and a 6–31G* basis set for all other atoms [25]. The IEF-PCM (integral equation formalism polarizable continuum model) for solvent effects (chloroform) was also used [26]. For calculating some ion-pair complexes, we have chosen initial guess geometries of Styryl-9⁺ with one or two counteranion(s) (tetramethylborate $\text{B}(\text{Me})_4^-$) positioned in the vicinity of the benzothiazolinium position. Time-dependent DFT (TD-DFT) with a hybrid functional B3LYP, as also implemented in Gaussian 09, was used to calculate optical absorption. In the simulated spectrum, a Gaussian spectral smearing of 2500 cm^{-1} was used.

3. Results and discussion

3.1. Formation of organic Styryl-9 nanoparticles and their spectroscopic properties

A series of organic Styryl-9 nanoparticles dispersed in aqueous solution were successfully synthesized by the “ion association” method [22,23]. The size and morphology of the synthesized Styryl-9 nanoparticles examined by STEM observations are shown in Fig. 1. The STEM images reveal that the samples have the particle diameters in the range of 30–50 nm ($\rho = 1$) and 20–30 nm ($\rho = 3$). As the ρ increases, the particle size slightly decreases. This behavior is quite similar to that observed for various kinds of cyanine

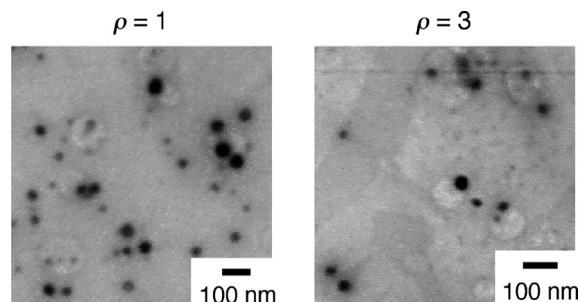


Fig. 1. Typical STEM images of the Styryl-9 nanoparticle samples prepared at $\rho = 1$ and 3.

Download English Version:

<https://daneshyari.com/en/article/6492948>

Download Persian Version:

<https://daneshyari.com/article/6492948>

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