



# The interaction of fluorescent Pyronin Y molecules with monodisperse silver nanoparticles in chloroform

Ayşe Merve Şenol, Önder Metin \*\*, Murat Acar, Yavuz Onganer, Kadem Meral\*

Department of Chemistry, Faculty of Science, Atatürk University, 25240 Erzurum, Turkey

## ARTICLE INFO

### Article history:

Received 26 May 2015

Received in revised form

29 July 2015

Accepted 29 September 2015

Available online 3 October 2015

### Keywords:

Xanthene dyes

Pyronin Y

Silver nanoparticles

Fluorescence lifetime

Quantum yield

## ABSTRACT

The interaction of fluorescent Pyronin Y (PyY) molecules with monodisperse silver nanoparticles (Ag NPs) in chloroform was studied by using UV–Vis, steady-state and time-resolved fluorescence spectroscopies. Monodisperse Ag NPs were synthesized by using a surfactant assisted organic solution phase protocol comprising the tandem thermal decomposition and reduction of silver (I) acetate in oleic acid and oleylamine at 180 °C. The average particle size of Ag NPs was determined to be ~3 nm by transmission electron microscopy (TEM) and their X-ray diffraction (XRD) pattern revealed the face centered cubic crystal phase. Afterward, PyY and monodisperse Ag NPs were interacted in chloroform via sonication at various time periods. The obtained spectroscopic results revealed that the photophysical properties of PyY molecules were dramatically changed after their interaction with Ag NPs in chloroform. It was determined that the amount of Ag NPs and PyY has the major effects on the photophysical properties of the dye.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Transition metal nanoparticles (NPs) have been gained a great interest by the scientist owing to their unique properties compared to the bulk materials [1]. Among the transition metal NPs, noble metal NPs such as Ag (silver) and Au (gold) have generated great interest in many fields such as photonics and biological sensing owing to their strong surface plasmon resonance (SPR) in visible region [2]. Ag NPs are especially the most studied and best established systems for waveguides, surface enhanced Raman scattering (SERS) and antibacterial applications etc. In this regard, various methods have been reported for the synthesis of Ag NPs [3–6], but a few of them yielded to Ag NPs with controllable size and morphology [7]. The synthesis of monodisperse Ag NPs has a crucial role, since the size and morphology of Ag NPs have great effect on their physical and chemical properties. For example, the optical properties of Ag NPs can be altered by using a synthesis method yielding the size and morphology controlled Ag NPs [8].

On the other hand, organic dye molecules have gained a great deal of attention in electronics and optoelectronics due to their low

cost and easy design at nanoscale. Pyronin Y, which is a xanthene derivative and positively charged organic compound, is one of the widely-studied one among the organic dyes. One important phenomenon for dye molecules is the dye aggregation. The dye aggregation plays a key role in many technological applications such as photographic industry, photosensitization, molecular optoelectronic devices, light-harvesting biological systems and nonlinear optical materials due to their unique optical behaviors [9–12]. It is reported that PyY can be exposed to molecular aggregation processes [13–15]. More recently, it is demonstrated that the photophysical properties of PyY can be affected by their interaction with other materials [16]. For example, graphene oxide, clays, polyelectrolytes and metallic NPs are commonly used changing the photophysical properties of dye molecules in liquid media [13–16]. It is known that the fluorescence intensity of dye molecules is quenched or enhanced in the close proximity of metallic NPs via energy transfer or electron transfer. The quenching of fluorescence dominates over enhancement at shorter distances and it is attributed to the efficient nonradiative energy transfer between the dye molecule and the metallic NPs [17–19]. For the applications containing metallic NPs and dye molecules, it is vital to understand photophysical behavior of dye molecules in presence of metallic NPs.

In the present study, we report a study of interaction between PyY molecules and monodisperse Ag NPs in chloroform. After

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [ometin@atauni.edu.tr](mailto:ometin@atauni.edu.tr) (Ö. Metin), [kadem@atauni.edu.tr](mailto:kadem@atauni.edu.tr) (K. Meral).

treatment of PyY molecules with Ag NPs in chloroform via sonication, the photophysical behaviors of the dye were followed by UV–Vis, steady-state fluorescence and time-resolved fluorescence spectroscopy techniques. The experimental results revealed that monodisperse Ag NPs caused partially the formation of dye aggregates of PyY along with changing its photophysical properties.

## 2. Experimental

### 2.1. Materials

PyY, silver (I) acetate (Ag(Ac)), oleic acid (OAc), oleylamine (OAm), 1-octadecene (ODE), isopropanol, ethanol, chloroform and hexanes were purchased from Sigma–Aldrich and used as it is.

### 2.2. Synthesis of Ag NPs

Monodisperse Ag NPs were synthesized by using a surfactant assisted organic solution phase protocol comprising the tandem thermal decomposition and reduction of silver (I) acetate in OAc and OAm at 180 °C [20]. In a typical synthesis, 170.0 mg Ag(Ac), 1.0 mL of OAm, OAc and 10.0 mL of ODE were mixed and stirred at 700 rpm under continuous nitrogen flow in a special four-necked reactor that allows to temperature control via a thermocouple within the reactor. The resulted mixture was heated up to 60 °C slowly and kept at this temperature for 5 min. Next, the resulted solution was further heated to 180 °C by a heating rate of 2–3 °C and maintained at this temperature for 20 min. Then, the mixture was cooled down to 40 °C and centrifuged at 9500 rpm for 15 min after the addition of isopropanol into the each nanoparticle solution separated into two centrifuge tubes. Ag NPs were redispersed in hexanes and centrifuged again at 9500 rpm for 15 min after the addition of ethanol. Finally, Ag NPs were stored in hexanes (in dark) (Scheme 1).

### 2.3. Quantum yields

Fluorescence quantum yields ( $\phi_f$ ) of the samples were calculated by making comparison with a reference dye (Rhodamine 101,  $\phi_f = 1.0$  in ethanol). The method applied for the determination of fluorescence quantum yields were described elsewhere [21]. The radiative ( $k_r$ ) and nonradiative ( $k_{nr}$ ) deactivation rate constants were calculated according to method described elsewhere [17].

## 2.4. Instruments

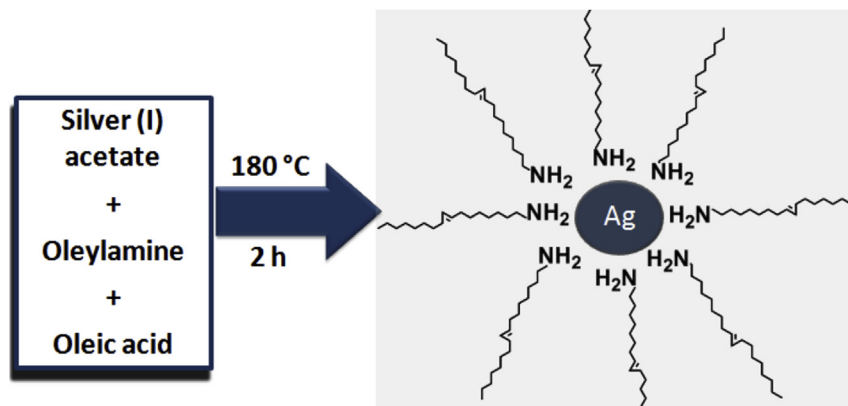
Transmission electron microscopy (TEM) images were recorded on a FEI Technai G<sup>2</sup> Spirit BiO(TWIN) at 120 kV. X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer with Cu K $\alpha$  radiation (30 kV, 15 mA,  $\lambda = 1.54051 \text{ \AA}$ ) over a  $2\theta$  range from 20° to 80° at room temperature. Absorption spectra were recorded with a Perkin–Elmer (Model Lambda 35) spectrophotometer at room temperature, which is 1.0 cm  $\times$  1.0 cm quartz cuvette. Steady-state fluorescence spectra were taken with Shimadzu RF-5301 PC Spectrofluorophotometer. A Laser Strobe Model TM-3 lifetime fluorophotometer from Photon Technology International (PTI) was used to measure fluorescence lifetimes.

## 3. Results and discussion

### 3.1. Characterization of Ag NPs

Monodisperse Ag NPs were prepared by using a surfactant-assisted organic solution phase protocol comprising tandem thermal decomposition and reduction of Ag(ac) in OAm, OAc and ODE at 180 °C. In the synthesis recipe, OAm served as both surfactant and mild-reducing agent, OAc was acted as co-surfactant, and ODE was used as solvent. The recipe yielded monodisperse Ag NPs that were characterized by TEM, XRD and UV–Vis spectroscopy. Fig. 1A showed a typical TEM image of Ag NPs from which the formation of spherical nanoparticles with the average particle size of 3 nm was concluded. The formation of silver metallic particles was further confirmed by the XRD pattern (Fig. 1B). It shows broad peaks at  $2\theta = 38.4^\circ, 44.3^\circ, 64.5^\circ$  and  $77.1^\circ$  that are readily assigned to the 111, 200, 220 and 311 reflections of a face centered cubic (fcc) symmetry of metallic silver (JCPDS Silver, File No: 04–0783). However, the broad peaks indicates the very small crystallite size of Ag NPs.

The absorption spectroscopy is one of the most significant tools for the characterization of Ag NPs due to their surface plasmon resonance peak in visible region. Fig. 2 showed the UV–Vis absorption spectra of PyY, Ag NPs and PyY–Ag NPs (PyY@Ag NPs) in chloroform. Ag NPs showed a characteristic broad plasmon resonance peak at 431 nm. PyY ( $1.0 \times 10^{-5} \text{ M}$ ) in chloroform had two absorption peaks appeared at 551 (monomer band) nm and 540 nm (dimer band), when it had an absorption peak at 552 nm along with a slight absorption shoulder at  $\sim 540 \text{ nm}$  in the presence of Ag NPs. The effect of Ag NPs on the absorption property of PyY in chloroform was examined by comparing those absorption spectra. It was concluded that the presence of Ag NPs in chloroform modified the absorption characteristic of PyY (Fig. 2). While the dimer formation



Scheme 1. Synthesis of monodisperse Ag NPs.

Download English Version:

<https://daneshyari.com/en/article/1409099>

Download Persian Version:

<https://daneshyari.com/article/1409099>

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