Dyes and Pigments 91 (2011) 225–230

Contents lists available at ScienceDirect

Dyes and Pigments

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

Metal enhanced fluorescence of the fluorescent brightening agent Tinopal-CBX near silver island film

Hirdyesh Mishra [a], Yongxia Zhang [a], Chris D. Geddes [a,b,*]

[a] Institute of Fluorescence, University of Maryland Baltimore County, 701 East Pratt Street, Baltimore, MD 21202, USA
[b] Department of Chemistry, University of Maryland Baltimore County, 701 East Pratt Street, Baltimore, MD 21202, USA

ARTICLE INFO

Article history:
Received 14 July 2010
Received in revised form
21 February 2011
Accepted 4 March 2011
Available online 17 March 2011

Keywords:
Metal-enhanced fluorescence
Optical brightener tinopal-CBS
Surface plasmons
Plasmon enhanced fluorescence
Surface plasmon enhanced fluorescence
Photostability

ABSTRACT

Metal-enhanced fluorescence (MEF) studies of the optical brightener Tinopal-CBS (4,4′- distyrylbiphenyl sulfonic sodium salt) have been undertaken using steady-state and time resolved fluorescence measurements on silver island films (SiFs) deposited on glass slides and silver nano-particles adsorbed onto cellulose based filter paper. Nearly a 4.5 fold enhancement in fluorescence intensity is observed from both SiFs and nano-particle deposited cellulose filter paper. In addition an enhanced photostability and decrease in decay time is also observed on SiFs. These results are consistent with two distinct mechanisms of MEF, firstly coupling and transferring of the excited states energies of fluorophores to surface plasmons in the silver island deposited glass films, and secondly, an electric field enhancement effect, which facilitates enhanced absorption of the fluorophores. Our findings reveal significant benefits of enhanced luminescence and prolonged photostability of Tinopal CBS. As such, Plasmon-tinopal constructs offer new material opportunities as well as multifarious applications in the life sciences.

1. Introduction

Recently in the advancement of near-field spectroscopy, the metal-enhanced fluorescence (MEF) technology [1–3] has become a powerful tool to investigate the structure and dynamics of molecules near-to metallic nano-particles i.e. in the near field. Due to surface plasmons interactions, the photo-physical properties of molecules are found to be both drastically and favorably changed in ways which enhance emission and improve fluorophores photostability.

Over the last several years Geddes and coworkers [4–7] have developed a mechanistic interpolate as well as numerous applications of MEF from various metallic surfaces. In MEF, in addition to the enhancement in fluorescence, decreases in decay times and increases in photo stabilities along with angular-dependent emission are also frequently observed. Our current interpretation of MEF has been underpinned by a model whereby non-radiative energy transfer occurs from excited fluorophores to surface plasmons in non-continuous films, Scheme 1.

Tinopal-CBS is a fluorescent whitening agent and widely used to improve the appearance of various commercial products viz. washing powder, plastics, paper, paints, textile etc. [8–12] In addition, tinopal is also used in the clinical biosciences to detect human fecal contamination in water [13], rapid recognition of pulmonary dirofilariasis [14], Peroral infection of nuclear polyhedrosis virus [15] in bio-pesticides to understand the growth of crops [16], studying the behavior of pollinators [17–19] in soil spray analysis [20] and cellulose fiber analysis [21], to name but just a few examples. Tinopal-CBS is a sulfonic sodium salt of 4,4′- distyrylbiphenyl which readily absorbs UV radiation and emits a strong blue fluorescence in the wavelength range from 400 to 550 nm [13]. In the present paper, we report the dramatic change observed in the photophysics of Tinopal-CBS on silver islands deposited on both glass slides and also adsorbed onto silver nanoparticles deposited cellulose filter paper demonstrating significant further utility of tinopal-CBS. About ≈4.5 fold enhancement in far-field tinopal fluorescence is observed with near-field enhancement values about 50 fold grater, i.e. 225-fold as compared to a control sample containing no silver.

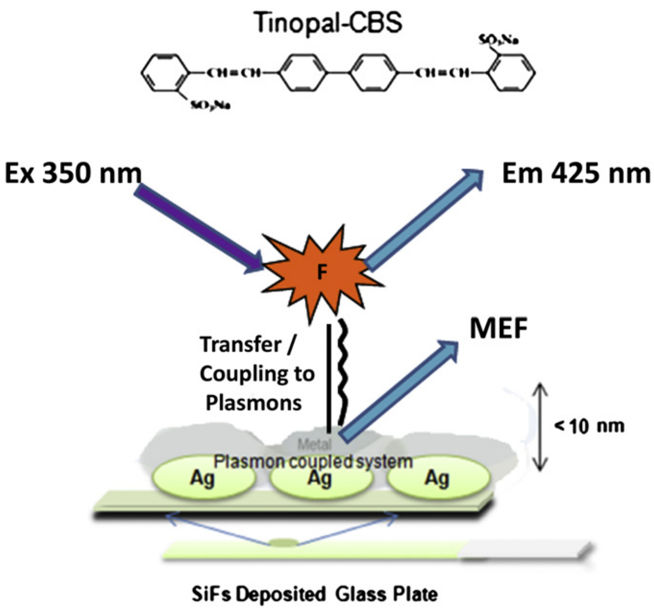
2. Experimental section

2.1. Materials

Tinopal-CBS was purchased from Tokyo Kasei Kogyo .Co. Ltd, Japan. Silane-prep glass microscope slides, Silver nitrate (99.9%),

* Corresponding author. Institute of Fluorescence, University of Maryland Baltimore County, 701 East Pratt Street, Baltimore, MD 21202, USA. Tel.: +1 410 576 5720; fax: +1 410 576 5722.
E-mail address: geddes@umbc.edu (C.D. Geddes).

0143-7208/$ – see front matter
doi:10.1016/j.dyepig.2011.03.005



Scheme 1.

sodium hydroxide (99.996%), ammoniumhydroxide (90%), D-glucose, ethanol (HPLC/ spectrophotometric grade), were purchased from Sigma–Aldrich Chemical company (Milwaukee, WI, USA). Quartz (75 mm × 25 mm) slides were purchased from Ted Pella Inc. CA, USA. The synthesis of silver colloids and SIFs were prepared according to previously published procedures [2]. The synthesis of silver colloids was undertaken using the following procedure: 2 ml of 1.16 mM trisodium citrate solution was added drop wise to a heated (90 °C) 98 ml aqueous solution of 0.65 mM silver nitrate while stirring. The mixture was heated for 10 min, and then cooled in ice until use. This procedure yields ca. 50 nm silver colloids as confirmed by TEM analysis. Three hundred micro-liters of tinopal dissolved in water was sandwiched between both the quartz slides and the SIFs coated quartz slides, respectively. Tinopal in water solution was subsequently pipetted onto the Ag colloid dried paper for the paper studies also.

Instrumentation Absorption spectra of tinopal on blank glass substrates and SiFs films were collected using a single beam Varian Cary 50-Bio UV-vis spectrophotometer. Emission spectra were collected using a Varian Cary Eclipse fluorescence spectrophotometer having a pulsed xenon source for excitation. A front face sample geometry was used to undertake all the fluorescence measurements with a slit width of 5 nm, both in the excitation monochromater and emission monochromater channels. Fluorescence decays were measured using a Horiba Jobin Yvon Tem-Pro fluorescence lifetime system employing the time-correlated single photon counting (TCSPC) technique, with a TBX picosecond detection module. The excitation source was a pulsed LED source of wavelength 372 nm having maximum repetition rate 1.0 MHz and pulse duration 1.1 nanosecond (FWHM). The intensity decays were analyzed by decay analysis software (DAS) version 6.4 in terms of the multi-exponential model: $I(t) = \sum_i \alpha_i \exp(-t/\tau_i)$ where α_i are the amplitudes and τ_i are the decay times, $\sum_i \alpha_i = 1.0$. The fractional contribution of each component to the steady state intensity is given by The values of α_i and τ_i were determined by nonlinear least squares impulse reconvolution analysis with the goodness of fit judged by the residual, autocorrelation function and χ^2 values. The measurement error in decay time analysis was of the order of 0.01 ns. Photo-stability experiments where undertaken using a 405 nm laser coupled with a neutral density filter and Ocean optics spectrophotometer HP2000. Real-color photographs of the fluorescence emission were taken through an emission filter with a Canon Power shot S50 Digital Camera. AFM images were performed on a Molecular Imaging Picoplus Microscope. Samples were imaged at a scan rate of 1 Hz with 512 × 512 pixel resolution in contact mode.

3. Results and discussions

SiFs are sub-wavelength size silver particles formed by reduction of silver nitrate on a glass surface. The absorption spectra of silver islands (SiFs) deposited for different times on glass slides are shown in Fig. 1(a). A broad structured absorption spectra ranging from 300 to 800 nm, having an absorption maximum at ≈ 380 nm is observed. On increasing the SiFs deposition time, the optical density of these films typically increases as shown in the inset of Fig. 1(a), along with slight change in structure. This indicates an increase in SiFs density on

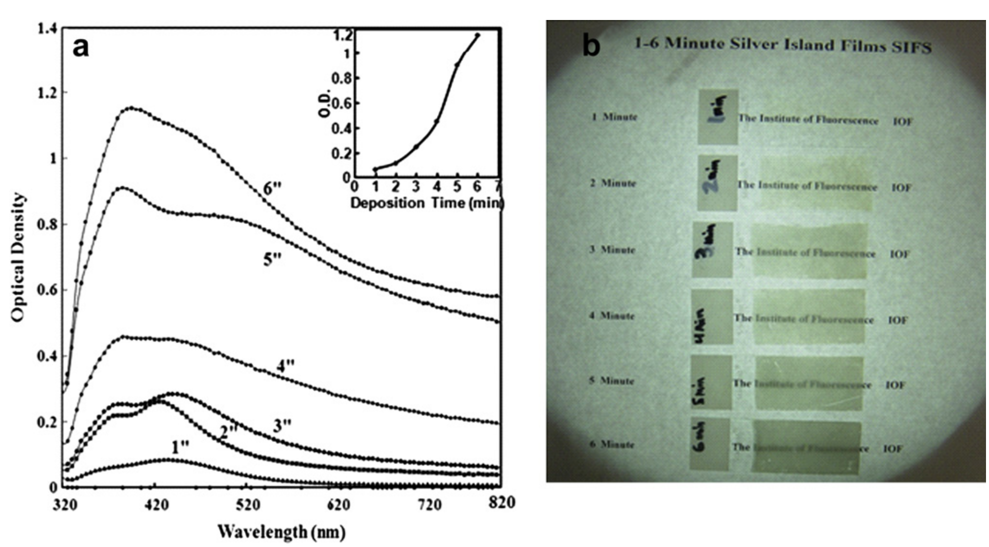


Fig. 1. (a) Absorption spectra and (b) Photograph of SiFs deposited on glass slides for different silver deposition times in minutes.