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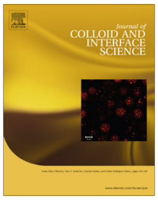

Dual emission from 2-(4′-*N*,*N*-dimethylaminophenyl)pyridoimidazole–nanoparticle composite: Effect of β-cyclodextrin

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The interactions of the silver nanoparticles with 2-(4′-*N*,*N*-dimethylaminophenyl)benzimidazole and its nitrogen substituted analogues, 2-(4′-*N*,*N*-dimethylaminophenyl)pyridoimidazoles are investigated by absorption, steady-state and time resolved fluorescence, field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM) techniques. The surface plasmon resonance band, the FESEM and the TEM images of the particles suggest that the fluorophores can stabilize the nanoparticles even in the absence of any other stabilizing agent. On the other hand, in the absence of fluorophores the nanoparticles are unstable and coagulate. In contrary to the earlier literature reports that interactions of nanoparticles with intramolecular charge transfer (ICT) or twisted intramolecular charge transfer (TICT) species quenches their fluorescence, to the best of our knowledge, the first ever formation of TICT state by interactions of nanoparticles with the fluorophores is observed. The formation of TICT state in 2-(4′-*N*,*N*-dimethylaminophenyl)pyridoimidazoles results in dual emission. The TICT emissions from the nanoparticle-fluorophore complexes are weak. But the emissions become prominent upon complexation with β-cyclodextrin.

1. Introduction

Nanoparticles–fluorophores interactions have been gaining interest in recent years due to their wide applications in various fields [1–3]. Metal nanoparticles can enhance or quench the molecular fluorescence by energy transfer. In addition, electron transfer may compete with energy transfer and quench molecular fluorescence. Lian et al. [2] have shown that the emission of rhodamine B is quenched predominantly by electron transfer and energy transfer is a minor process. The size and the shape of the nanoparticles, distance between the fluorophores and the nanoparticles, the anchoring groups (such as –SH, $-NH_2$) on the nanoparticles and the nature of the localized surface plasmon resonance (SPR) of the nanoparticles may play major role in determining the dominating process [3–18]. Zerbetto et al. [3] observed that the distance between the nanoparticles and the fluorophores plays an important role in the energy transfer efficiency. Separated gold nanoparticles were found to be more efficient in energy transfer from fluorophores inside silica matrix than the aggregated ones. The energy transfer from rhodamine 6G to gold nanoparticles depend on the size and shape of the particles [14]. Zuilhof et al. [15] reported that the shortest alkyl chain separation results in most efficient energy transfer between amine terminated silicon nanoparticles and ruthenium bipyridine complex. Li et al. [17] studied the effect of core nanoparticles on the fluorescence enhancement of cationic conjugated polymer attached to it. They showed that the silica nanoparticles that contain the silver core were more efficient in enhancing the fluorescence of polymer than those without silver core. The system was proven to be effective for cellular imaging due to its low toxicity. Singh and Strouse [18] demonstrated that overlap of the local surface plasmon resonance plays an important role in the energy transfer between dye and gold nanoparticles those were separated by double stranded DNA.

In energy transfer, the excitation energy of the excited donor is transferred from donor to the acceptor due to overlap of the fluorescence spectrum of donor and the absorption spectrum of the acceptor. In charge transfer, the electronic charge is transferred from the donor to acceptor. The charge transfer between the fluorophore and the nanoparticles has also attracted enormous research attention, especially in the context of dye sensitized solar cells [19–22] and photocatalysis [23,24]. Photoinjection of electrons from (E)-3-(5-((4-(9H-carbazol-9-yl)phenyl)ethynyl)thiophen-2-yl)-2-cyanoacrylic acid to TiO_2 occur through a multiexponential electron injections mechanism, where the slower component was the intramolecular charge transfer (ICT) state [25]. Ziolek et al. [26] illustrated that the charge transfer dynamics of triphyenylaminecyanoacrylic acid sensitized TiO_2 nanoparticles, nanotubes, and

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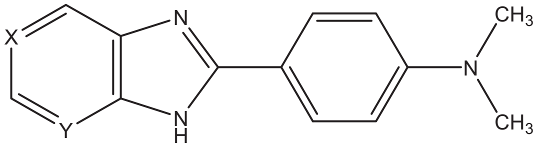
nanorods takes place via the electron injections with a picosecond electron injections component. Fakis et al. [27] have revealed similar multiexponential electron injections in dye-sensitized TiO_2 nanoparticles. Ultrafast electron injections were reported for most of the organic dye-sensitized TiO_2 nanoparticles but multiexponential and picosecond components of electron injections were observed for inorganic dye-sensitized TiO_2 nanoparticles [28–35]. Hyun et al. [36] studied the charge transfer rate from PbS nanocrystals to ligand molecules and illustrated that it increases dramatically with solvent dielectric constant.

Biologically active molecules, 2-(4′-N,N-dimethylaminophenyl)imidazo[4,5-b]pyridine (DMAPIP-b, Fig. 1) and 2-(4′-N,N-dimethylaminophenyl)imidazo[4,5-c]pyridine (DMAPIP-c, Fig. 1) are interesting fluorophores [37–40]. Earlier studies [41–44] suggested that both molecules can act as probe to study various environments. DMAPIP-b as well as DMAPIP-c exhibit dual emission. However, unlike other twisted intramolecular charge transfer (TICT) emitting fluorophores [45,46], they emit dual emission only in protic environment and pyridyl nitrogen plays an important role in the process [37–40]. As mentioned above, the interactions of nanoparticles with fluorophores may result in charge transfer that lead to quenching of the ICT/TICT state. Conversely, if the charge transfer to nanoparticles leads to the formation of TICT state, it will produce dual emission from DMAPIP-b and DMAPIP-c. TICT emission is much more sensitive to environment than normal emission. Therefore, it can be used for probing, sensing and imaging biological and other complex environments. In addition due to dual emission nature, the presence of TICT emission allows these types of fluorescent nanomaterials to be used as ratiometric probes for different applications. The measurements ratiometric sensing will eliminate the error due to photobleaching, uneven loading etc. in these applications. Therefore, to find whether nanoparticle can induce dual emission we have investigated the interactions of DMAPIP-b and DMAPIP-c with silver nanoparticles. For better understanding, we also examined the interactions of nanoparticles with 2-(4′-*N*,*N*-dimethylaminophenyl)benzimidazole (DMAPBI, Fig. 1), which has no pyridyl nitrogen.

2. Materials and methods

The synthetic procedure to obtain DMAPBI, DMAPIP-b, DMAPIP-c were reported elsewhere [37,38,47]. The silver nano particles were prepared by the reduction of silver ions by *N*,*N*-dimethylformamide (DMF), in the absence of stabilizing agents by the procedure reported by Pastoriza-Santos and Liz-Marzán [48]. 100 μL of fluorophore solution (1 mM) in methanol was taken and dried at 50 °C. The nanoparticle concentrations were varied by adding different amount of nanoparticle solution to the dried fluorophore and made up to 10 ml. Silver nitrate (0.1 mM) was used as a source for silver. HPLC grade DMF procured from Spectrochem India was used as received. β-cyclodextrin (β-CD) from Sigma–Aldrich, USA was used as received and the concentration of β-CD was 15 mM in DMF. All the spectral measurements were made at 10 μM concentrations of the fluorophores.



X = Y = CH **DMAPBI**

X = CH, Y = N **DMAPIP-b**

X = N, Y = CH **DMAPIP-c**

Fig. 1. Structures of DMAPBI, DMAPIP-b and DMAPIP-c.

Varian Carry 100 and Jobin Yvon Spex Fluoromax-4 were used to record the absorption and the steady state fluorescence spectra, respectively. Time resolved fluorescence was measured by Edinburgh Instruments Life Spec-II instrument. A 375 nm laser diode was employed as the excitation source with Hamamatsu microchannel plate (MCP) as detector. Using a software provided by Edinburgh Instrument, the fluorescence decays were analyzed by reconvolution method.

TEM measurements were performed using a JEM 2100 (Jeol, Peabody, MA) machine operating at a maximum accelerating voltage of 200 kV. 5 μL of sample drop was coated onto a carbon coated copper TEM grid followed by air drying and the resulting grid was then analyzed under TEM. FESEM measurements were carried out in a Carl Zeiss, SIGMA VP instrument. Typically, a 10 μL drop of each sample was deposited on an aluminum foil covered glass slide, dried, sputter-coated with gold film using a sputter coater (SC7620“Mini”, Polaron Sputter Coater, Quorum Technologies, Newhaven, England), and imaged using FESEM.

3. Result and discussion

3.1. Growth and stabilization of the nano particles

The nanoparticles were allowed to grow in the absence and the presence of fluorophores. The growth was followed by SPR band (∼420 nm) of silver nanoparticles (ESM). In absence of fluorophores the absorbance of the SPR band decreases with time. On the other hand in the presence of fluorophores, the absorbance of the SPR band increases and it follows the order DMAPIP-b > DMAPIP-c > DMAPBI. While DMAPBI and DMAPIP-c assist the growth of the nanoparticles for several hours, DMAPIP-b facilitates the nanoparticles to grow even up to 10 days. The absorption spectrum of the nanoparticles in presence of DMAPBI is broader compared to those in the presence of DMAPIP-b and DMAPIP-c. The full width at half maximum in the presence of DMAPBI, DMAPIP-b and DMAPIP-c are ∼10,500 cm^{-1}, 7000 cm^{-1} and 7700 cm^{-1}, respectively. Depending upon the stabilizing capacity of fluorophores different numbers of nanoparticles are formed. This is also suggested by the difference in absorbance value of the SPR band of the particles.

The FESEM images and the photographs of the vials containing nanoparticles are presented in (Fig. 2). In the absence of fluorophores, after 24 h all the silver particles stick on the glass surface and the solution becomes transparent. The FESEM image also confirms the absence of nanoparticles in the solution. This result is consistent with the study reported by Pastoriza-Santos and Liz-Marzán [48] where silver nanoparticles in the absence of stabilizer electro statically attach onto the glass surfaces and only very small amount of particles disperse in the solution [48]. However, in presence of the fluorophores, silver particles do not stick on the side of the wall even after 24 h and it is substantiated by FESEM (Fig. 2) and TEM images (ESM). TEM images also indicate that the average size of the particles grown in presence of DMAPIP-b is relatively smaller than those grown in the presence of DMAPIP-c. These results clearly establish that the fluorophores interact with the nanoparticles and the interactions lead to stabilization of the nanoparticles. The stabilization depends on the presence and the position of the pyridyl nitrogen. Imidazopyridines stabilize the nanoparticles more than DMAPBI and it follows the order DMAPIP-b > DMAPIP-c > DMAPBI. In other words the pyridyl nitrogen plays an important role in these interactions and the stabilization of the nanoparticles.