Journal of Molecular Liquids 272 (2018) 198–208

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Photoinduced electronic interactions between acridine derivatives and small gold nanoparticles: A spectroscopic insight

Chaitrali Sengupta [a,1], Piyali Mitra [c,1], Shruti Chatterjee [d], Gourab Bhattacharjee [e], Biswarup Satpati [e,2], Samita Basu [b,*,2]

[a] Department of Chemical, Biological and Macromolecular Sciences, S.N. Bose National Centre for Basic Sciences, Block JD, Sector III, Salt Lake, Kolkata 700098, India
[b] Chemical Sciences Division, Saha Institute of Nuclear Physics, HBNI 1/AF, Bidhannagar, Kolkata 700 064, India.
[c] Department of Materials Science, Indian Association for the Cultivation of Science, Kolkata 700 032, India.
[d] School of Bioscience, Indian Institute of Technology, Kharagpur, Kharagpur 721302, India
[e] Surface Physics and Material Science Division, Saha Institute of Nuclear Physics, HBNI, Kolkata 700 064, India.

ARTICLE INFO

Article history:
Received 1 June 2018
Received in revised form 13 September 2018
Accepted 17 September 2018
Available online 19 September 2018

ABSTRACT

The central tricyclic moiety of acridine derivatives has fascinating redox properties. We take advantage of the electronic properties of two such acridine derivatives, 9-amino acridine (9AA-HCl) and acridine yellow, recognized so far as potential antimicrobial agents, since these drugs can act both as potential electron donor and acceptor, depending upon the reduction potential of its adjacent chemical entity. Precise timescale of formation of contact ion pair (CIP) and solvent separated ion pair in solution involving donors and acceptors has been much encountered and debated in literature till date. In our present communication, we like to decipher the mechanism and timescale of individual steps of photoinduced electron transfer (PET) between these drugs and gold nanoparticles (AuNPs) with dimension of 3-5 nm, which is important and presently our subject of interest since AuNPs could be used for shuttling of electrons between different donor and acceptor moieties. Steady-state and time-resolved absorption and fluorescence studies evidently reveal the signature of PET both in singlet and triplet states. Using ultrafast time-resolved fluorescence techniques we have tried to quantify precisely the time required for formation of CIP which is within fs-ps time regime. Moreover, 9AA-HCl, being a planar molecule, dimerises at excited state in presence of high concentration of AuNPs, due to its immobilisation over their surface. The occurrence of excited state proton transfer in triplet state for 9AA-HCl-AuNPs conjugate is depicted by laser flash photolysis experiments. The presence of all such charge transfer channels, provokes us to delineate the intricacies of the mechanisms involved which would help further to evaluate the possibility of making devices for energy storage using these drugs.

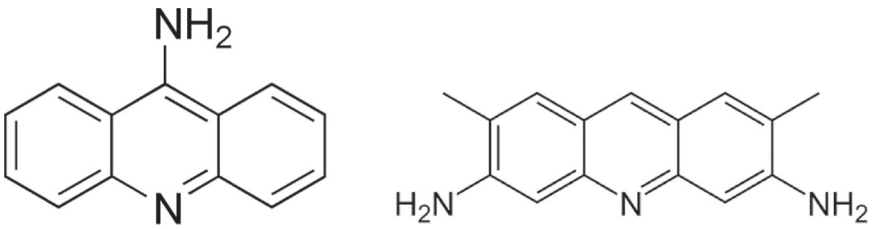
1. Introduction

Nowadays the interactions of organic molecules with metal nanoparticle surface intrigue the researchers primarily for its two faceted aspects. The one is to understand the interaction between the organic and inorganic interface in a nanohybrid from a fundamental level and the other is to apply the functionalisation of nanoparticle to be used for several purposes e.g., photovoltaic devices, photothermal therapy, SERS experiments, biosensing, etc. [1]. Although there are many published papers where the syntheses of organic capped gold nanoparticles are highlighted, yet there are limited number of reports available till date which help in understanding the exact modes of interactions. However, (A) intermolecular interactions, (B) energy transfer, (C) electron transfer, and (D) emission from the chromphores bound on the metal nanoparticles are the possible deactivation pathways of those excited fluorophores bound to gold nanoparticles. With a specific mention, it could be said, that direct binding of a fluorophore to the metal surface can result in quenching of excited states due to electron transfer between the chromophore and the gold surface [2–4], which has been confirmed from photocurrent measurements by several groups [5,6]. Development of biological tracers and optoelectronic devices necessitates the modification of gold nanoparticles with different fluorophores [7,8]. Moreover, luminescence of a number of fluorophores is quenched when they are in close proximity to the surfaces of gold nanoparticles. This effect can be used for several sensor approaches.

The metal nanoparticles are optically transparent, act as dipole and have close lying bands with freely moving electrons [9,10]. The light absorption properties of nanoparticles vary with their size. Small gold nanoparticles of 5 nm diameter do not show any plasmon absorption, of

* Corresponding author.
E-mail address: samita.basu@saha.ac.in (S. Basu).
[1] Both the authors contribute equally.
[2] HBNI

https://doi.org/10.1016/j.molliq.2018.09.080
0167-7322/



Scheme 1. Chemical Structure of Acridine derivatives.

5–50 nm gold nanoparticles show a sharp absorption band in the 520–530 nm region [11,12]. The metal particles of silver, gold and copper show distinct and well-defined plasmon absorptions in the visible region.

The AuNPs interact with a large number of therapeutically important drugs, and among these, acridine based drugs are known to be efficient fluorophores and are often used as photosensitizers in photodynamic therapy (PDT), which is actually based on the concept of preferential accumulation of photosensitizers in the unwanted cells those are irradiated with visible light in the presence of oxygen. Researchers indicate that the planarity of tricyclic core of acridine derivatives (Scheme 1) is an important factor affecting their ability to intercalate into DNA, which inhibits the cell cycle and/or induces cell death [13].

The most important fluorophores belonging to the family of acridines are 9-amino acridine hydrochloride hydrate (9AA-HCl), acridine Yellow (AY), acridine Orange (AO) and proflavine (PF). Among them, 9AA-HCl belongs to those rare classes of compounds which readily form dimer at higher concentration (~10^{-2} M) [36] and exists in neutral, singly protonated and doubly protonated forms.

Our present work is an endeavour to study the interactions of two acridine based drugs with thiocyanate capped small sized AuNPs in homogeneous aqueous medium with the help of steady state and time resolved absorption and fluorescence spectroscopic as well as transmission electron microscopic techniques. 9AA-HCl possesses a tricyclic core with one amine moiety and AY is an acridine with two amine moieties. Deciphering the exact mechanism of interaction between these acridine drugs and small AuNPs is our present challenge. However, acridine drugs are very well known as electron donor and acceptor depending on the reduction potential of adjacent chemical entity. Therefore, in our current investigation, we have chosen 9AA-HCl and AY to explore the mechanism and direction of charge transfer with AuNP, as we presume that small sized AuNPs could render a suitable platform to delineate the mode of binding of these two derivatives of acridine with varying steric and electronic properties.

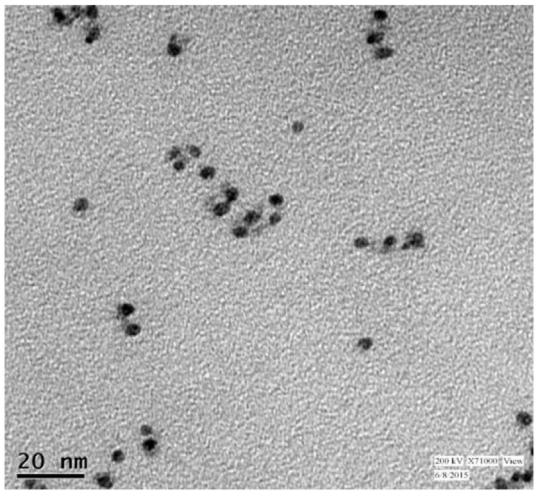


Fig. 1. Transmission electron micrographs of AuNP colloids with an average particle of size of 3–5 nm.

1.1. Experimental section

The compounds, 9AA-HCl, AY and $HAuCl_4$, $3H_2O$ are purchased from Sigma–Aldrich and used without further purification. The structures of 9AA-HCl and AY are given Scheme 1.

Water is triply distilled before use. Solutions are prepared by dissolving measured amount of all chemicals in triple distilled water by volumetric method.

Preparation of gold nanoparticles:

The gold colloids in this case are prepared by the conventional thiocyanate reduction of $HAuCl_4$ in water with sodium thiocyanate at room temperature [8]. The TEM micrographs have confirmed the particle diameter of these gold nanoparticles to be 3–5 nm.

Absorption and fluorescent measurements

JASCO V-650 absorption spectrophotometer and Spex Fluoromax-3 Spectro-fluorimeter have been used to record steady-state absorption and fluorescence spectra of 9AA-HCl, AY and 3-5 nm gold nanoparticle respectively using a 1.0 cm path length quartz cuvette. For a particular sample, the wavelength of absorbance maximum (λ_{max}) has been used as excitation wavelength for the associated emission scan. Time-resolved emission spectra of 9AA-HCl and AY are obtained using a picosecond pulsed diode laser based time-correlated-single-photon counting fluorescence kinetic spectrometer with λ_{ex} ~377 nm and and λ_{ex} ~471 nm respectively and MCP-PMT as a detector in absence and presence of AuNP [14,15]. The emission from the samples is collected at right angle to the direction of the excitation beam which maintains magic angle polarization (54.7•) and a bandpass of 2 nm. The full width at half maximum (FWHM) of the instrument response function is 270 ps. The resolution of the instrument is 28 ps per channel. Data analysis software (IBH DAS 6.2) has been used to fit the data to exponential functions after deconvolution of the instrument response function by an iterative reconvolution technique. Here, reduced chi square (χ^2) and weighted residuals serve as parameters for goodness of fit. All the steady-state and time-resolved measurements are performed at room temperature (298 K).

Femtosecond fluorescence up-conversion measurements

Femtosecond fluorescence up-conversion setup (FOG-100, CDP Corp.) has been used for the measurement of the lifetime of fluorescence transients of the order of picosecond. The sample has been excited at 400 nm with full excitation slit width using the second harmonic of a mode-locked Ti-sapphire laser (Mai Tai Spectra Physics). This is pumped by a 5 W Millennia (Spectra Physics). A nonlinear crystal (1 mm BBO, $\theta = 25$•, $\varphi = 90$•) has been used to generate second harmonic. Magic angle configuration has been maintained to obtain the fluorescence emitted from the sample and up-converted in another