

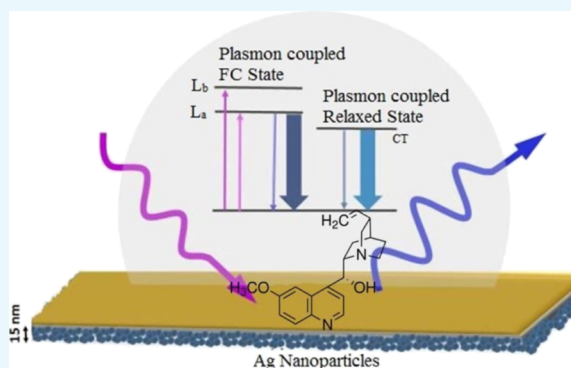
Excited-State Dynamics of Quinine Sulfate and Its Di-Cation Doped in Polyvinyl Alcohol Thin Films Near Silver Nanostructure Islands

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ABSTRACT: The present study demonstrates the near-field effect of silver nanostructure island films (SNIFs) on the photophysics and excited-state dynamics of quinine sulphate (QS) and its di-cation (QSD), doped in polyvinyl alcohol (PVA) films. The results indicate a nearly 3.8-fold enhancement in absorption and 4000-fold enhancement in fluorescence in SNIF-coated QS-doped PVA films, whereas only twofold enhancement in absorption and sevenfold enhancement in fluorescence intensity are found in SNIF-coated QSD-doped PVA films. However, an increase in photostability and a decrease in decay time have been observed in both the SNIF-coated films as compared to their uncoated forms. Further, a decrease in the magnitude of the edge excitation red shift in emission spectra along with a red shift in the L_a band and a rise in the intensity of the L_b band of excitation is observed in SNIF-coated QSD films because of strong coupling of the L_b band with the surface plasmons of silver nanoparticles. Moreover, X-ray photoelectron spectroscopic measurement of silver nanoparticle-coated QS–PVA films shows no change in $3d_{3/2}$ and $3d_{5/2}$ transitions of silver, whereas the decrease in energy in these silver transitions in the QSD–PVA system is observed as compared to silver nanoparticle-coated PVA films. These results indicate the formation of a field-governed radiating plasmon and plasmon-coupled unified fluorophore system, respectively. This affects the photophysics of both of the molecules by plasmonic coupling of the Frank–Condon state, solvent relaxation state, and charge-transfer state by different orders of magnitude.



1. INTRODUCTION

The surface plasmon's interaction of metallic nanoparticles with fluorophores drastically and favorably changes the photophysics^{1–4} and bioactivity^{5–8} of the molecules. The collective oscillations of surface electrons of metallic nanoparticles regulate the confinement of excitation and emitted radiation, which is accountable for the strange properties of such metallic nanomaterials. On changing the shape and size of these nanoparticles, the plasmonic band can be tuned with the absorption band of a nearby fluorophore, which controls the fluorescence dynamics of it through the near-field effect.^{9–12} The distinctive physicochemical properties of such hybrid nanomaterials lead to the development of chemosensors^{13–16} and biosensors¹⁷ for diagnosis and treatment of diseases,^{18,19} detection of pathogenic agents,^{20,21} drug delivery,^{22–25} and so forth. As nanosized metallic particles show toxicity in a variety of organisms, these nanoparticles may constitute a toxicological risk, being generally more toxic than bulk²⁶ and plasmon resonance-enhanced photoelectrodes' and photocatalysts' activity.²⁷ Therefore, the study of the interaction of nanomaterials with drug molecules is significant because of their induced toxicity that would modify some specific biological functions in living systems.²⁸ However, the toxicological risk will be reduced in hybrid or functionalized nanomaterials.

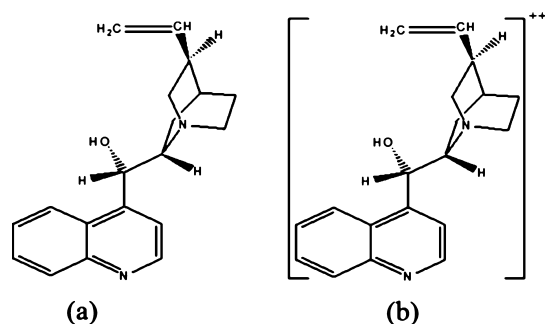
Contemporary research has witnessed the emergence of metallic nanoparticle-coated drugs as more effective drugs. Among the heterocyclic compounds, quinoline derivatives (cinchona alkaloids) are of great interest owing to their pharmaceutical and industrial applications.²⁹ Therefore, the study of their spectral and photophysical properties near the surface or interface of metals holds significance. A few studies of quinine sulphate (QS) and its derivatives have been reported for their use as an optical sensing material for halides and some metal ions.⁸ The past few decades have witnessed extensive studies being carried out on photophysics and photochemistry of QS in bulk liquids^{30–35} and some restricted environments.^{36–41} The protonated species of QS (QSD) shows a red shift in both the absorption and emission spectra with respect to QS, which is attributed to perturbations of the $\pi-\pi^*$ and $n-\pi^*$ states.²³ The molecular structures of QS and QSD molecules are presented in Scheme 1. QSD is found to be more photostable, more immune toward oxygen-quenching, and to have a high fluorescence quantum yield [$\phi = 0.55$] owing to its stable circular structure.³⁰ The time-domain fluorescence measurement of QS at ambient temperature

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Scheme 1. Molecular Structure of (a) QS and (b) QSD



shows dual decay time τ_1 and τ_2 in a nanosecond timescale, which corresponds to a two-state model. However, QSD also shows dual decay time, in which τ_2 increases with increase in monitored wavelength of emission spectra because of the solvent relaxation process, whereas τ_1 exhibits a rise time behavior, which also resembles a two-state model with a negative amplitude of the decay time in the red edge of the emission wavelength.

Meech and Phillips³³ have reported the nonexponential decay of QSD with the emission wavelengths because of a change in the charge density distribution and geometry of the molecule. Further, in a temperature-dependent steady-state and time-domain fluorescence measurement of QSD from 80 to 290 K, Pant et al.³⁴ proposed two major relaxation processes to understand this complex fluorescence dynamics of QSD, first, a charge-transfer process which occurs around 160 K and second, a solvent reorientation process taking place in the liquid phase. Interestingly, QSD is one of the exceptional emitters in which excited-state solvent relaxation occurs in a nanosecond timescale even at room temperature. Therefore, time-resolved emission spectroscopy and other dynamic studies, which depend on solvent relaxation, could easily be made using QSD as an emitter.³⁵ However, these characteristics show that QSD cannot be used as a fluorescence lifetime standard. Further, some unusual characteristics of QSD in emission and excitation spectra, viz. polarization and the bathochromic shift in the emission spectrum on excitation at the red edge of the first absorption band and the excitation spectrum of QS is not found mirror image of the absorption spectrum, suggested that the emission arises simultaneously from two close-lying states.^{42,43} On excitation at the red edge of the absorption band, only certain configurations are excited, resulting in a red-shifted emission, which lacks some high-frequency components compared to emission because of short-wavelength excitation. Fletcher⁴⁴ has postulated that the edge excitation red shift (EERS) effect which arises because of the solvent bonding to the chromospheres restricts the position of the auxochrome to at least two average conformers, having its own distinct electronic transition probabilities. However, the excitation dependence of the emission of polar aromatic molecules in viscous polar solvents is not a common phenomenon, and it is related to the microenvironmental heterogeneity.^{45,46} Generally, the EERS of a probe molecule is used for detection of free volume in the polymer matrix,⁴² and is a powerful tool to monitor the organization and dynamics of membranes, micelles, and reverse micelles.⁴³ Mishra et al.⁴⁷ reported a decrease in the EERS, fluorescence lifetimes, time-dependent fluorescence Stokes shift, and fluorescence depolarization in concentration-dependent studies of QSD ions in an

aqueous medium and suggested that the energy migration among the QSD ions along with solvent relaxation is responsible for this process. The appearance of the change of the EERS in QSD in different protic/aprotic polymers,³⁹ and micelles,⁴⁷ indicates that the QSD molecule is very sensitive for surface or interface studies and can also be used as a probe to investigate the mobility of solvent molecules around the excited molecules.

The present work describes the effects of the plasmons of silver nanostructure island films (SNIFs) on the excited-state dynamics and photophysics of QS and its di-cation, QSD, doped in a polyvinyl alcohol (PVA) polymeric matrix. Since the dynamics of charge transfer (CT), solvent relaxation and magnitude of EERS of QS and QSD depend upon the polarity and free volume of the polymer matrix. Therefore, the present study will enable us to understand the near field effect of SNIF on these excited state relaxation processes, which affect the fluorescence dynamics of these molecules at the surface/interface of silver nanoparticles in the restricted free volume and microenvironment.

2. RESULTS AND DISCUSSION

The photophysical experimental measurement and finite-difference time-domain (FDTD) calculation⁴⁹ shows that a nearly 20 nm thin layer of silver over silica nanoparticles gives maximum enhancement in emission intensity. Therefore, in the present study, only a 20 nm thin Ag film with a deposition rate of 1 Å/s has been deposited over the PVA film. The morphology of the SNIF over the PVA film was obtained by using field-emission scanning electron microscopy (SEM, Quanta-200) and atomic force microscopy (AFM, NT-MTD, Russia), respectively, as shown in Figure 1.

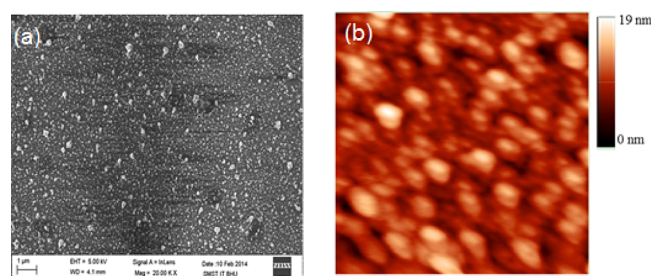


Figure 1. (a) SEM and (b) AFM images of 20 nm SNIFs [size $2 \mu\text{m} \times 2 \mu\text{m}$].

2.1. Steady-State Absorption and Fluorescence Measurements. Overlapped absorption, fluorescence, and decay curves of QS and QSD molecules doped in PVA thin films with and without silver nanoparticle coating are shown in Figure 2. QS doped on the PVA film shows absorption band maximum at 335 nm along with a hump at 325 nm, which corresponds to L_a and L_b transitions, respectively, in the QS molecule having $\pi \rightarrow \pi^*$ characteristics along with other two higher electronic-state transitions lying between the 200 and 300 nm range at 240 and 280 nm. A nearly 3.8-fold enhancement is observed in this absorption band in the silver nanoparticle-coated QS-doped PVA film [Figure 2a] with respect to the uncoated QS-doped PVA film. Further, an increase in optical density at the red edge of the absorption band is also observed in SNIF-coated films. In the case of the QSD-doped PVA film, the L_a band is red-shifted and observed

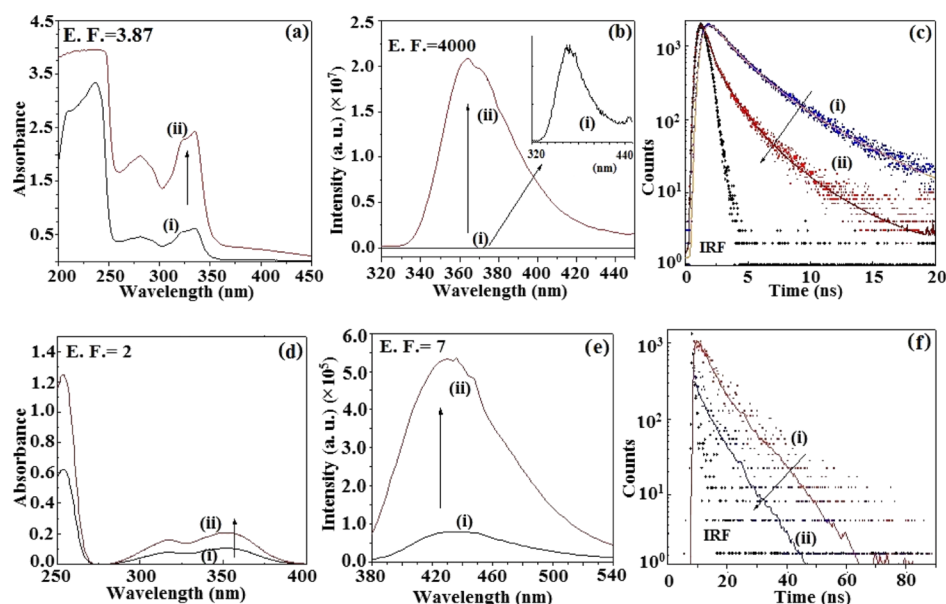


Figure 2. Overlapped absorption (a, d), emission (b, e), and decay curves (c, f) of QS- and QSD-doped PVA films (i) without and (ii) with silver SNIF coating.

at 352 nm, whereas the L_b band is found to be blue-shifted and observed at 317 nm, along with other two higher electronic transition states lying in at 220 and 250 nm, similar to the QS-doped PVA film. Further, only about twofold enhancement is observed in L_a and L_b absorption bands in the SNIF-coated QSD-doped PVA film [Figure 2d] with respect to the QSD-PVA film without SNIF coating. The enhancement in the absorbance of QS and QSD is observed because of the enhanced near-field effect of SNIFs by interaction of the incident photon flux. The changes in the magnitudes of enhancement in the absorbance of QS and QSD molecule are due to different modes of interactions of the photon flux with these two molecules near the SNIF, which is consistent with X-ray photoelectron spectroscopic measurements.

In the fluorescence spectrum, the QS-doped PVA film shows a very weak fluorescence band at 365 nm upon excitation by 340 nm [inset of Figure 2b]. In the SNIF-coated QS-doped PVA film, this fluorescence band intensity enhances nearly 4000-fold, under the same condition, without changing the shape or structure of the fluorescence band, though a blue shift is observed having the magnitude of ~ 20 Å as shown in the normalized spectrum [Figure 3a]. The enhancement factor is defined as the ratio of intensity observed in the SNIF-coated sample film divided by that from a PVA control substrate under identical conditions. The QSD-doped PVA film shows a red-shifted fluorescence band, observed at 450 nm as shown in Figure 2e with respect to the QS-doped PVA film, but in the SNIF-coated QSD-doped PVA film, this fluorescence band intensity enhances only sevenfold along with a blue shift of about 60 Å nm as shown in the normalized spectrum [Figure 2b]. The observed blue shift is similar to the previously reported results in metal-enhanced fluorescence (MEF) because of a change in the dipole moment.⁵⁰ Further, the blue shift in the fluorescence band of QSD is found to be greater than QS in the SNIF-coated film.

2.2. Time-Domain Fluorescence Measurements. The analyzed overlapped decay curves of both QS- and QSD-doped PVA films, with and without SNIF coating, are shown in Figure 2c,f, respectively, and the corresponding fitted decay data are

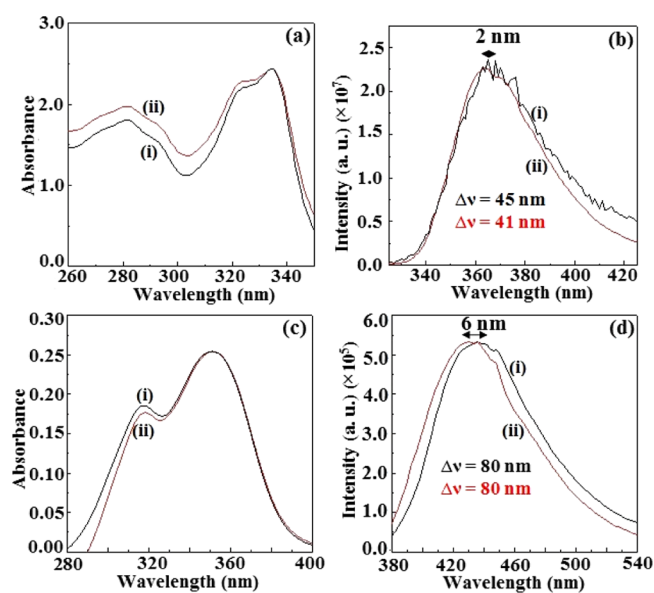


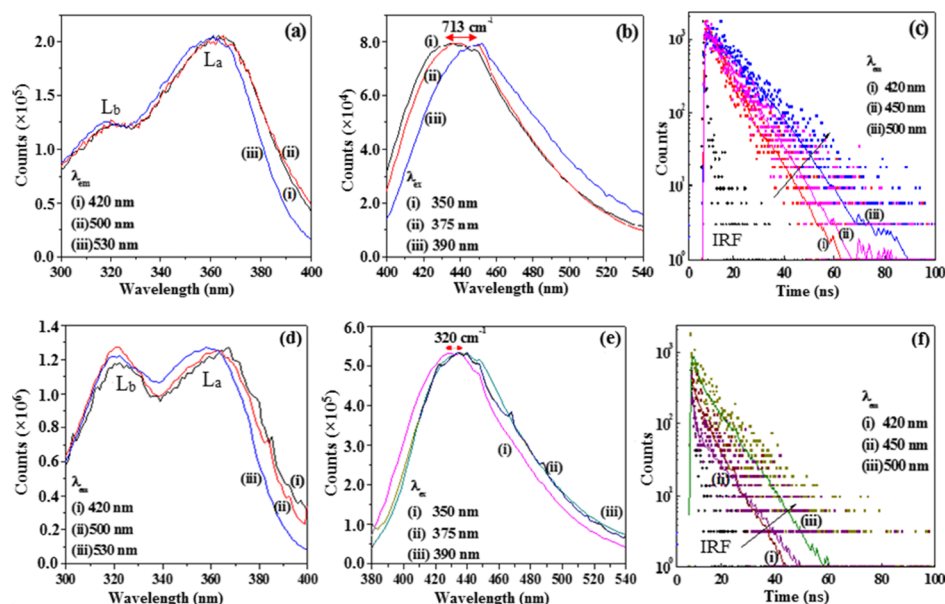
Figure 3. Visualization of normalized absorption spectra of (a) QS and (c) QSD; normalized emission spectra (b) and (d) QSD [QS- and QSD-doped PVA films (i) without and (ii) with SNIF coating].

presented in Table 1. As evident from the results, the fluorescence decay of both the QS and QSD reduces in SNIF-coated films with reference to the uncoated QS or QSD PVA films.

The QS doped in the PVA film shows a fluorescence peak at 365 nm, which decays double exponentially with decay times of 1.42 and 4.32 ns. In SNIF, the decay curve of QS doped in the PVA best fitted in the triple exponential decay function, and both the magnitude and amplitude of these decay parameters (i.e., 1.35 and 3.55 ns) decrease with respect to the SNIF-coated sample with the appearance of an additional short decay time of ~ 0.02 ns. Further, an average decay time of 3.01 ns and an amplitude-weighted value of about 0.07 ns have been calculated for QS. These values are reduced to 0.88 and 0.29 ns, respectively, in SNIF-deposited PVA films. The

Table 1. Fitted Decay Parameter of the QS and QSD Doped in the PVA Film with and without SNIF at 400 nm; $\lambda_{\text{ex}} = 375$ nm

molecule		τ_1 (ns)	α_1	τ_2 (ns)	α_2	τ_3 (ns)	α_3	$\langle\tau\rangle$	τ	χ^2
QS	without coating	1.43 ± 0.02 (45%)	0.022	4.32 ± 0.05 (55%)	0.009			0.07	3.01	1.208
	with coating	0.02 ± 0.00 (51.7%)	0.882	1.35 ± 0.05 (37%)	0.008	3.55 ± 0.22 (10.3%)	0.001	0.03	0.88	1.213
QS di-cation	without coating	2.39 ± 0.79 (3%)	0.022	8.28 ± 0.57 (39%)	0.093	17.68 ± 0.58 (58%)	0.065	1.97	13.60	1.013
	with coating	0.96 ± 0.12 (7%)	0.104	6.77 ± 0.26 (32%)	0.070	16.12 ± 0.26 (61%)	0.055	1.45	12.05	1.078

**Figure 4.** Overlapped (a) excitation spectra [emission monitored at different emission wavelengths], (b) emission spectra [excited by different wavelengths], and (c) decay curves [decay monitored at different wavelengths] of QSD-doped PVA films. Overlapped (d) excitation spectra [emission monitored at different emission wavelengths], (e) emission spectra [excited by different wavelengths], and (f) decay curves [decay monitored at different wavelengths] of QSD-doped PVA films coated with SNIF.

decrease in the magnitude of the decay parameters along with an increase in fluorescence intensity in the presence of SNIF indicates the plasmonic coupling of Frank–Condon (FC) and relaxed (R) excited state of the free space component of QS with SNIF nanoparticles. However, the appearance of an additional very short decay time component indicates the proximity of the QS to the SNIF, which is consistent with reports on the fluorescence of other fluorophore intensities near silver nanoparticles. The appearance of the additional fast decay channel supports the blue shift of fluorescence in the presence of SNIFs.

However, the QSD doped in the PVA film decays triple exponentially, having a decay time of 2.39, 8.28, and 17.68 ns, respectively. Further, a long decay component of 17.68 ns along with two short decay components correspond to FC and relaxed state as in the case of the QS-doped PVA film. It indicates two major relaxation processes, viz., a charge-transfer process and a solvent reorientation process, which occurs in the polymeric medium.⁴⁷ Furthermore, in SNIF, these three decay times of QSD reduce in a similar trend to QS in PVA, which again indicates plasmonic coupling of the FC state, relaxed-excited state, and CT state with SNIF nanoparticles. The increase in the amplitude of the short decay time component and a decrease in the amplitude of the long decay time component again supports the blue shift of fluorescence in the presence of SNIF. The reduction in decay times in the presence of SNIF indicates the coupling of excited states of QS with plasmons of the SNIF and the subsequent nonradiative energy transfer from both the excited state of QS to metal

particles, which is consistent with the previously proposed MEF model.⁴⁸ In essence, the reduced lifetimes are because the metal itself radiates the coupled quanta with the very short lifetime, decreasing the amplitude-weighted excited-state lifetime.

2.3. EERS Emission Spectral Measurements. In order to have an insight into the effect of plasmons of SNIF on the photophysics of red edge excitation for both kinds of QSD-doped PVA films (i.e., with and without SNIF coating) measurements were performed. The measured excitation spectra, by monitoring emission at different wavelengths, emission spectra, excited by the different wavelengths of the red edge of the absorption band, and decay profile at different emission wavelengths (are provided in Figure 4). Normalized excitation spectra of QSD in the PVA matrix are shown in Figure 4a, which shows a small blue shift in the L_a band with no change in the position and intensity of the L_b band on monitoring the emission spectra at 400, 500, and 530 nm.

However, in the case of SNIF-coated QSD-doped PVA films, for the same monitored emission wavelengths, a large blue shift in the L_a band and an increase in the intensity of the L_b band is observed (Figure 4d) as compared to the uncoated sample. In the case of the EERS emission spectra, a shift of ~ 713 cm^{-1} is observed in QSD fluorescence spectra doped in the PVA films as shown in normalized emission spectra (Figure 4b), on exciting the sample from 350, 375 and 390 nm, respectively, whereas the magnitude of EERS is found to be decreased up to 320 cm^{-1} in the case of the SNIF-coated

QSD-doped PVA matrix. Further, in time domain measurements, a regular increase in the magnitude of three decay times is observed, on monitoring the decay toward the red edge of the emission spectra of the QSD-doped PVA matrix both with and without SNIF coating (Figure 4c,f). However, a reduction in all the three decay times is observed in the SNIF-coated QSD film throughout the emission profile with respect to the QSD-doped PVA film.

Similar effects of a change in intensity and shift in fluorescence emission toward a longer wavelength in the fluorescence characteristics of QSD doped in sol–gel glasses filled with solvent after poly(methyl methacrylate) impregnation were compared previously.⁵¹ These changes were explained by the free volume available within polymer films. The broad distribution-function model,^{39,47} representing various species which are not interconvertible during the lifetime of the solute, shows the presence of EERS of QSD in glass and polymeric media. However, it could not explain the absence of any rising portion in the decay of these media. Therefore, the presence of multicomponent decay can be explained because of the trapping of the molecule in different geometries. However, the absence of negative amplitude does not rule out the possibility of excited-state CT. In the broad distribution model, the multicomponent decay curve can be well fitted in two or three components. It has been reported that the decay of QSD in the compact aprotic polymer film and dried Nafion film becomes triple exponential.³⁹ The additional decay time is found to be 10 ns, which may be due to the presence of a fraction of QSD molecules which are bonded to the polymer chain at a higher viscosity site. As mentioned earlier, in fluid media the EERS can be rationalized by the fact that the excitation of the solute is accompanied by a large change in dipole moment and the solvent reorientation time is not fast enough to bring the molecule to the relaxed state during the decay time.

On the other hand, EERS in the frozen glass at 80 K can be explained by the trapping of the molecule in different geometries.³⁴ Therefore, free volume effect also plays an important role in explaining the kinetics of adsorbed molecules. On increasing the rigidity of the film, it will reduce the free space available for the molecules and restrict their motion. This causes increase in both decay time and fluorescence intensity. However, in the QSD-doped PVA polymer matrix in the presence of SNIF, there is a decrease in EERS. Probably, the molecules are oriented in a particular direction, hence restricting their motion in the free space available in the PVA matrix. Further, the increase in absorbance of the L_b band in the presence of SNIF may be due to a strong coupling of surface plasmons of SNIF with the polarized transition state along the bonds (L_b) because of the interaction of photon flux. The blue shift in the L_a band of the QSD molecule in the presence of SNIF is due to near-field-induced change in the dipole moment.

2.4. Photostability Measurements. To understand the change in magnitude of MEF in QS- and QSD-doped polymer films coated with SNIF with respect to uncoated films, the photostability of these films were also measured. These films were exposed to the light of wavelength 350 nm from a 150 W xenon lamp for about 900 s, and the change in fluorescence intensity at 400 nm was measured as a function of time as depicted in overlapped photostability curves in Figure 5. The photostability of the QS is found to be more pronounced with respect to QSD on the SNIF-coated PVA film as compared to

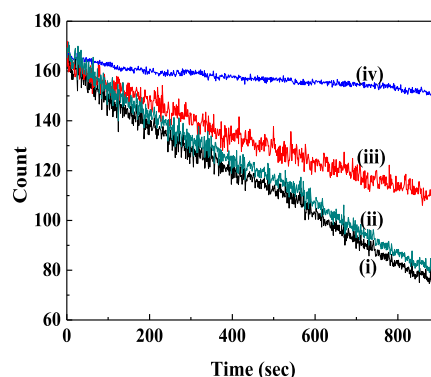


Figure 5. Overlapped photostability curves of the (i) QS- and (ii) QSD-doped PVA film in the absence of SNIF, whereas (iii) and (iv) show photostability of QSD and QS in the presence of SNIFs.

the reference sample films (without silver coating). The observed results of enhanced fluorescence photostability are consistent with the shortening of the decay time of QS and QSD near SNIF as proposed in the MEF model.⁴⁸

2.5. X-ray Photoelectron Spectroscopy Measurements of Silver Near the QS- and QSD-Doped PVA Film. To understand the huge change in the encasement factor of absorbance and fluorescence intensity of QSD with respect to QS, X-ray photoelectron spectroscopy (XPS) measurement was carried out. The overlapped XPS spectra of thermally deposited over QS and QSD (with and without coating) are shown in Figure 6. Silver shows binding energy transitions:⁴³

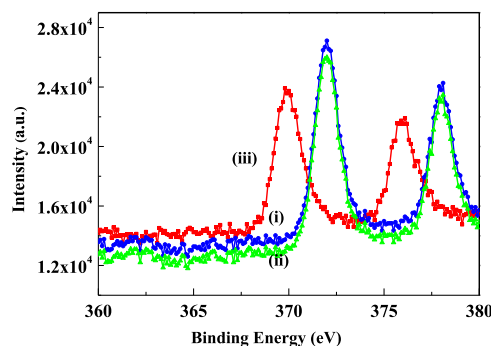
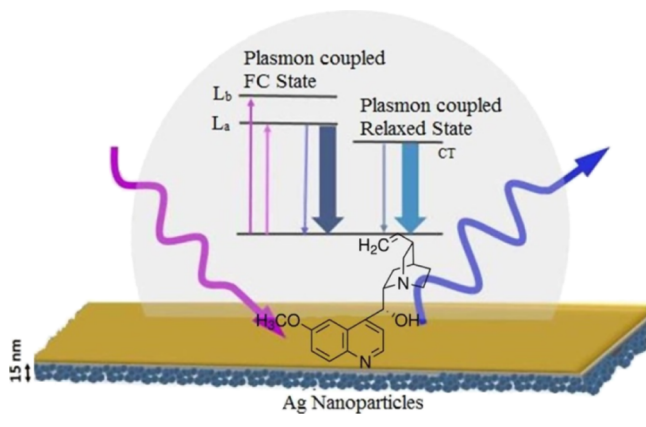


Figure 6. X-ray photoelectron spectra of thermally coated 10 nm thick silver nanoparticles on the (i) PVA film (ii) QSD-doped PVA film and (iii) QS-doped PVA film.

$3d_{3/2}$ and $3d_{5/2}$ at 378 and 372.5 eV, respectively, in the bare SNIF-coated PVA film (Figure 6i). It is also clear from Figure 6ii that there is no change in the binding energy transitions of Ag in the SNIF-coated QS-doped PVA film, whereas the binding energy of both the transition of silver is decreased along with a decrease in intensity in the QSD-doped PVA film coated with SNIF (Figure 6iii) as compared to the bare SNIF-coated PVA film. The observed results confirm the creation of a fluorophore–plasmon coupled integrated system of the QSD-doped PVA film with silver nanostructures, by chemical-adsorption (via weak van der Waals forces). In this unified system, partial CT from QSD to SNIF takes place and causes a drop in the binding energy and induces very less enhancement in fluorescence intensity. However, in the case of the QS-doped PVA film, no change in binding energy indicates the formation of a field-controlled radiating plasmon-fluorophore unified system.

Thus, because of the field effect of surface plasmon coupled fluorescence, a huge enhancement in the absorption/fluorescence band and a decrease in decay time is observed along with an increase in photostability. The current understanding of MEF is supported by a model, according to which the nonradiative energy transfer occurs from excited fluorophores (dipoles) to surface plasmons in noncontinuous films. Coupling of the surface plasmons of SNIF with the FC-state and relaxed-excited state (R-state) is shown in Scheme 2.

Scheme 2. Cartoon Depicting the MEF of QS/QSD Because of Surface Plasmon-Coupled FC and R States



3. CONCLUSIONS

The present study shows that the photophysics and photochemistry of QS and its di-cation drastically change by the presence of silver nanostructures. Enhancement in the absorption, emission, photostability, and quenching in decay time confirms the coupling between surface plasmons of silver nanoparticles with the excited states of QS and its di-cationic species in PVA films. Further, in the case of the QS-doped PVA film, no change in the XPS spectrum indicates that field-induced surface plasmon coupling is responsible for the huge enhancement in fluorescence intensity; however, the red shift in the XPS spectrum in the case of the QSD-doped PVA film indicates the creation of the fluorophore–plasmon coupled unified system causing less enhancement in fluorescence intensity. Furthermore, in the QSD-doped PVA film, decrease in EERS and raise in absorbance of the L_b band in the presence of SNIF point out the formation of the fluorophore–plasmon coupled system and restricted motion of the QSD molecule in the free volume of the PVA matrix. Most significantly, the results show that near-field surface plasmons can enhance and govern the photophysics of neutral as well as di-cationic species of QS, which will have greater worth in the development of next-generation smart materials for diverse applications in pharmacy and industry.

4. EXPERIMENTAL SECTION

4.1. Materials. Quinine sulfate (QS) and PVA (molecular weight 9000) were purchased from Sigma-Aldrich. QS molecule-doped PVA films were prepared by mixing the required amount of PVA grains dissolved in hot water at 40 °C. The estimated concentration of different films is about 0.5 wt %. Purity was checked by a fluorescence run test of the neat polymer film. QSD-doped PVA films were prepared by mixing PVA grains with QS in 0.1 N H_2SO_4 and dissolving it in water.

The mass was spread in a propylene dish and dried in an incubator.

4.2. Construction of SNIFs. Vacuum thermal evaporation/deposition technique at 10^{-6} mbar using HIND HIVAC 12A4D was used to construct the SNIF over PVA film. In our previous work,⁴⁸ we had observed that the depositions of the ultrathin film (<7 nm) of Ag metals cause formations of quenched condense nanofilms with charge confinement ($T_s < 0.1T_m$, where T_s is substrate temperature during deposition and T_m is the melting point of Ag).

4.3. Instrumentation. Absorption spectra of QS- and QSD-doped PVA films on blank glass substrates and SNIF films were obtained using a double beam JASCO V-670 UV/vis spectrophotometer. Emission spectra were recorded by an Edinburgh fluorescence spectrophotometer having a 150 W xenon source for excitation. A front face sample was used to undertake all the fluorescence measurements with a slit width of 3 nm, both in the excitation monochromator and emission monochromator channels. Fluorescence decays were also measured by an Edinburgh fluorescence lifetime system FLS-920 instrument, employing the time-correlated single photon counting technique, with an R985 PMT detection module. The excitation source was a pulsed laser source of wavelength 375 nm having maximum repetition rate of 1.0 MHz pulse duration and 73.5 ps pulse width. The intensities of the decay curves were analyzed by associated decay analysis software regarding the multiexponential model

$$I(t) = \sum_i \alpha_i \exp\left(-\frac{t}{\tau_i}\right)$$

where α_i 's and τ_i 's are amplitude and decay times, respectively and $\sum_i \alpha_i = 1.0$. The fractional contribution of each component to the steady-state intensity is given by

$$f_i = \frac{\alpha_i \tau_i}{\sum_j \alpha_j \tau_j}$$

The mean lifetime of the excited state is given by

$$\bar{\tau} = \sum_i f_i \tau_i$$

and the amplitude-weighted lifetime is given by

$$\langle \tau \rangle = \sum_i \alpha_i \tau_i$$

The values of α_i 's and τ_i 's were determined by nonlinear least squares impulse re-convolution analysis with the goodness of fit adjudged by the residual, autocorrelation function and chi square (χ^2) values. In decay time analysis, the measurement of the error was of the order of 0.01 ns. Photostability experiments were undertaken using a 150 W xenon lamp with a neutral density filter for 350 nm excitation and change in emission intensity recorded at 400 nm of the sample films with an Ocean optics spectrophotometer HP-2000 in a time scan of about 900 s. XPS measurements of the sample films were carried out with the help of Kratos Analytical, Shimadzu group company AMICUS XPS UK.

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Notes

The authors declare no competing financial interest.

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