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The impact of Au doping on the charge carrier dynamics at the interfaces between cationic porphyrin and silver nanoclusters

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Abstract

We explore the impact of Au doping on the charge transfer dynamics between the positively charged porphyrin (TMPyP) and negatively charged silver nanoclusters (Ag_{29} NCs). Our transient absorption (TA) spectroscopic results demonstrate that the interfacial charge transfer, the intersystem crossing and the triplet state lifetime of porphyrin can be tuned by the doping of Au atoms in Ag_{29} NCs. Additionally, we found that the electrostatic interaction between the negative charge of the cluster and the positive charge on the TMPyP is the driving force that brings them close to each other for complex formation and subsequently facilitates the transfer process.

Keywords: (Interfacial charge transfer • Nanoclusters • Intersystem crossing • Triplet state • Metal ion doping)

1. Introduction

A fundamental understanding of interfacial charge transfer at donor-acceptor interfaces is needed, as it is among the most important dynamical processes for optimizing performance in many light harvesting systems, including photovoltaics [1, 2] and photocatalysis. [3, 4] In general, the photo-generated singlet excitons in photoactive materials exhibit very short lifetimes because of their dipole-allowed spin radiative decay and short diffusion lengths. [5] In contrast, the radiative decay of triplet excitons is dipole forbidden; therefore, their lifetimes are considerably longer. [6] The possibility of modulating the charge transfer, intersystem crossing (ISC) rate and triplet state lifetime of organic molecules is among the greatest challenges to control or achieve. In this study, we have chosen cationic porphyrin as a good candidate for such a study because of its high photostability and exciting photophysical properties. [7-9] In addition, it is well known that the deactivation of porphyrin upon optical excitation in the Soret-band transition leads to either internal conversion to the lowest possible singlet excited state (S_1) or intersystem crossing (ISC) via between the S_1 and T_1 states, the rate of ISC and the spin-orbit coupling. [10]

The excited state lifetime of porphyrin can be modulated through charge transfer interaction in the

presence of different electron acceptors and carbon nanotubes. [11-13] Being in this regime, the noble metal nanoclusters can act as an excellent electron-acceptor component due to its distinct electronic structure that arises from precise numbers of metal atoms, with unique optical and photophysical properties. [14-16] The most widely studied metal nanoclusters are gold and silver and their different mixtures because of their potential applications in photovoltaics, photo-catalysis, bio-imaging, and sensing. [17, 18] Although the interactions of the porphyrin moiety with semiconductor nanoparticles have been studied, [19] porphyrin-metal nanocluster interaction and the possibility of modulating the triplet state lifetime and electron injection between them has never been discussed.

In this study, we have investigated the interfacial charge transfer dynamics in positively charged meso units of 5, 10, 15, 20-tetra (1-methyl-4-pyridino)-porphyrin tetra (p-toluene sulfonate) (TMPyP) and neutral 5, 10, 15, 20-tetra (4-pyridyl)-porphyrin (TPyP), with negatively charged undoped and gold (Au)-doped silver Ag_{29} NCs. The feasibility of electron transfer from the free porphyrin moiety to the cluster has been restrained based on energy level alignment, confirmed through emission quenching and transient absorption spectroscopic measurements. Different ground state bleaching (GSB) recovery and excited state absorption (ESA) decay of the porphyrin moiety in the presence of doped and undoped clusters has been observed, providing clear indication of the impact of Au ion doping on the deactivation mechanism of the excited porphyrin. Interestingly, we found that the

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triplet state lifetime of porphyrin is much longer in the presence of Au-doped Ag₂₉ NCs than undoped NCs, again demonstrating the impact of metal ion doping on the ISC and the spin-orbit coupling at porphyrin-Ag₂₉ NC interfaces.

2. Experimental Details

Materials. TMPyP were purchased from Sigma Aldrich and used without further purification. Ag₂₉ NCs were synthesized following the method reported in the literature. [20] Briefly, 8 mg of lipoic acid was dissolved in 5 mL of an ethanol: water mixture (3:1 v/v), and 0.05 mg NaBH₄ was added to the stirring solution after a minute. This step was followed by the addition of 200 μ L of a 25 mM solution of AgNO₃ and up to a 10-fold increase of NaBH₄ dropwise. The solution was continuously stirred for 5-6 hours, during which distinct color changes were observed. The Au-doped clusters were synthesized by replacing the AgNO₃ solution above with 1:10 molar HAuCl₄:AgNO₃ solution. The clusters were then precipitated by the addition of an equal volume of a 2:3 (v/v) mixture of methanol/acetonitrile solvent followed by centrifugation at 8000 rpm. This was repeated twice to remove excess ligand and the clusters were re-dispersed in water. Atomic precision of the clusters were confirmed by electrospray ionisation mass spectrometry.

Steady-State Measurements. Steady-state absorption and emission spectra were recorded on a Cary 5000 UV-visible spectrometer (Agilent Technologies) and a Fluoromax-4 spectrofluorometer (Horiba Scientific), respectively. The measurements were conducted in a rectangular quartz cell with a 1 cm optical path.

Femtosecond Transient Absorption (fs-TA) Spectroscopy. Femtosecond “fs” TA spectroscopy was performed on Helios spectrometers. The detailed experimental setup of the fs-TA can be found elsewhere. [21] Briefly, the setup employs a white-light continuum probe pulse generated in a 2-mm-thick sapphire plate using a small fraction of the fundamental output of a Ti: sapphire femtosecond regenerative amplifier operating at 800 nm with 35 fs pulses and a repetition rate of 1 kHz. Pump pulses at 650 nm were generated in an optical parametric amplifier (Newport Spectra-Physics). The pump and probe pulses were overlapped temporally and spatially in a 2-mm-thick cuvette cell containing the sample solutions. The probe light transmitted from the sample was collected and focused on a broadband UV-Vis detector to monitor the change in the absorbance (ΔA). The nanosecond transient absorption (ns-TA) spectroscopic measurement was also recorded following laser pulse excitation at 650 nm. The ns-TA spectra were measured using the pump-probe EOS setup, in which a standard probe beam is split into two: one travels through the sample, and the other is sent

directly to the reference spectrometer that monitors the fluctuations in the probe beam intensity. The EOS experimental setup is detailed elsewhere. [21]

3. Results and discussion

The absorption and fluorescence changes of TMPyP at a fixed concentration of 0.02 mM upon the addition of undoped and Au-doped Ag₂₉ NCs are shown in Fig. 1A-D.

Fig. 1 (A and C) Steady-state absorption and (B and D) emission (λ_{ex} = 515 nm) spectra of TMPyP with Ag₂₉ NCs (Top) and with Au-doped Ag₂₉ NCs (Bottom). The different colors represent the increment addition of NCs to TMPyP.

As previously reported, the intense Soret band (S_0 - S_2) of TMPyP was observed at 423 nm along with four Q-bands (S_0 - S_1) at 515, 555, 585 and 643 nm. [22] Upon the addition of Ag₂₉ NCs (Fig. 1 A and C), a decrease in the Soret-band intensity along with a spectral redshift of 12 nm was noticed, providing clear experimental evidence for the ground-state interaction between TMPyP and Ag₂₉ NCs. In contrast, a larger spectral redshift of 17 nm was noticed upon the addition of the same concentration of Au-doped Ag₂₉ NCs. This observation demonstrates that the metal ion doping strengthens the interaction between TMPyP and Ag₂₉ NCs. Interestingly, the four Q-bands transformed into two peaks at 572 and 640 nm. This result indicates the change in symmetry of the porphyrin macrocycle. [23] Since the Soret and Q-bands correspond to the electronic structure of the macrocyclic cavity of TMPyP, [24, 25] these observed spectral modifications are a strong indication of interactions between the macrocyclic cavity of porphyrin and Ag₂₉ NCs, adopting the same symmetry of the metalated porphyrin. Moreover, the strong TMPyP-Ag₂₉ NC interaction was also evidenced by quenching of the emission of TMPyP. Upon excitation

at 515 nm, free TMPyP exhibits a broad fluorescence band over the range of 625–800 nm, which corresponds to the S_1 – S_0 transition. The successive addition of equal concentrations of Ag_{29} NCs and Au-doped Ag_{29} NCs led to a spectral blue shift along with a decrease in the fluorescence intensity of TMPyP by almost 70% and 85%, respectively (Fig. 1 B and D). It should be noted that these changes are completely missing when we replace TMPyP with neutral porphyrin 10, 15, 20-tetra (4-pyridyl)-porphyrin (TPyP), as shown in Fig S1, ESI†. In other words, the successive addition of NCs up to 65 μ l into the TPyP solution has no effect on either the absorption or the emission spectra, providing a strong piece of evidence that the electrostatic interaction between the positively charged porphyrin and the negatively charged NCs is the main driving force for the ground- and excited-state interactions between TMPyP and NCs. This negative-positive charge cross-talk can form complexes on NCs surfaces via electrostatic interaction. [26] Furthermore, the different efficiencies for fluorescence quenching of TMPyP with the same concentrations of undoped and Au-doped NCs indicate that the heavy atom effect can act as an additional driving force to change the photophysics of TMPyP, including the ISC. It is worth mentioning that such quenching could also be a consequence of energy transfer from the TMPyP to NCs. However, we exclude this possibility because there is no spectral overlap between the absorption of the NCs and the emission of TMPyP.

As shown in Fig 2, the Raman spectra provide additional piece of evidence for the strong interaction between the porphyrin macrocycle and the surface of Ag_{29} NCs, as indicated by the distinctive differences between the Raman spectra of the free TMPyP and the TMPyP– Ag_{29} NCs assembly. The band at 332 cm^{-1} for TMPyP, which can be assigned to in-plane bending of the porphyrin core, disappears when Ag_{29} NCs are added. [27, 28] The TMPyP band at 402 cm^{-1} assigned to in-plane bending of the porphyrin core and pyridine ring, is shifted to 380 cm^{-1} with a strong shoulder band at 405 cm^{-1} in the TMPyP-NCs spectra, which confirms that the interaction takes place through the porphyrin cavity as well as with the pyridine ring. [11, 29] The in-plane bending of the pyridine ring band that appears in free porphyrin at 970 cm^{-1} also disappears when either undoped or Au-doped Ag_{29} NCs are added, confirming the strong interaction between the porphyrin macrocycle and the surface of the NCs. [30] The intensity drop of TMPyP band at 1298 cm^{-1} after the addition of NCs provides a clear indication for the change in molecular symmetry of TMPyP due to the complexation formation. [29]

Fig. 2 Raman spectra of (A) TMPyP and (B) its assembly with Ag_{29} NCs (C) with Au-doped Ag_{29} NCs using a laser wavelength of 473 nm. It should be noted that there is change relative intensity in the Raman bands which can be attributed to the binding of the porphyrin molecule to metal cluster.

As a final point, the Raman spectra of TMPyP with undoped and Au-doped Ag_{29} NCs provide solid evidence for a similar configuration to the metalation effect, supporting the steady-state absorption where the four-Q bands are transformed into two peaks. Similar results have been observed for TMPyP on the surface of ZnO nanoparticles. [30]

Femtosecond (fs) time-resolved laser spectroscopy can convey detailed information regarding the deactivation of the excited state in many chemical and material systems. [31–38] Therefore, we performed fs-transient absorption (TA) spectroscopic measurement with broadband capabilities and 120 fs temporal resolution. Upon analyzing the TA data (Figure 3) in a different time domains, the TMPyP in the absence of NCs shows a GSB approximately 423 nm and a broad ESA extending from 450 – 650 nm. The TA spectra for free TMPyP show minimal change over a 3-ns time window, which is expected based on the long lifetime of their singlet excited states, [39, 40] while the ones recorded with NCs exhibit fast changes, indicating rapid excited interactions in the singlet state. Moreover, while the TA spectra of TMPyP in the absence of NCs show the characteristic signal of porphyrin, [41] new spectral features (ground state bleach) are observed in their complexes with NCs in the range of 400–500 nm, which is consistent with the changes observed in the steady-state absorption.

Fig. 3 The fs-TA spectra of (A) free TMPyP (B) TMPyP + Ag₂₉ NCs (C) TMPyP + Au doped Ag₂₉ NCs in water after 650-nm excitation.

Interestingly, a new spectral feature is also observed in the range between 500-600 nm in the presence of NCs, which can be attributed to porphyrin cation radical TMPyP^{•+} resulting from electron transfer from TMPyP to NCs. [11] As shown in Fig. 3B and C, the formation of the cation radical is ultrafast (within 300 fs), which indicates that the electron transfer mechanism is static in nature.

To decipher the dynamics of the electron transfer process, kinetics traces were collected for the porphyrins with and without NCs, as shown in Figure 4. The cation radical band decays very fast in the presence of NCs due to the charge recombination. The kinetics at GSB and the radical band exhibit two time constants: one is very fast, a few picoseconds, due to charge recombination (CR), while the other is few nanoseconds and can be attributed to the lifetime of the unreacted porphyrin. In the presence of Au-doped Ag₂₉ NCs with TMPyP, the amplitude of the fast component is smaller, indicating an inefficient interaction compared with TMPyP-undoped Ag₂₉ NCs. One possible explanation for this difference may be the difference in optical band gap of the Au-doped Ag₂₉ NCs compared to the undoped Ag₂₉ NCs (Fig. S2, ESI[†]), which may create an energy offset in Gibbs free energy, the driving force for electron transfer. Thus, we have observed different kinetics of electron transfer from TMPyP to undoped and doped NCs. The other possible explanation for this difference is the difference in triplet state formation, which is very likely due to the heavy metal effect causing the singlet population, where the electron transfer occurs efficiently, to be greater in the case of undoped NCs.

Fig. 4 The fs-TA kinetic traces of (A) Excited State Absorption (ESA) monitored at 540 nm (B) Ground State Bleaching (GSB) monitored at 440 nm for free TMPyP (black), TMPyP + Ag₂₉ NCs (blue) and TMPyP + Au-doped Ag₂₉ NCs (green) in water after 650 nm laser excitation.

This mechanism is supported by the triplet state lifetime (see below). To investigate the triplet state behavior, ns-TA measurements were performed, and the time-resolved spectra of free TMPyP and of both doped and undoped TMPyP-NCs are given in Fig 5A-C.

Fig. 5 The ns-TA spectra of (A) free TMPyP, (B) TMPyP + Ag₂₉ NCs (C) TMPyP + Au-doped Ag₂₉ NCs in water after 650 nm laser excitation.

As shown, the TA spectra exhibit a GSB and a broad T_1 - T_n absorption, in agreement with the observations reported in the literature for the transient triplet state absorption. More specifically, the TMPyP exhibits a longer lifetime in the presence of undoped NCs, and GSB recovery proceeds more slowly compared to the free porphyrin shown in Fig 6. In the case of Au-doped NCs, the recovery is much slower than TMPyP both without and with undoped NCs, confirming the efficient triplet state formation due to the heavy metal effect. Specifically, free TMPyP exhibited a lifetime of 3.2 μ s, increasing to 32 μ s and 68 μ s in complexes of TMPyP with undoped Ag_{29} and Au-doped Ag_{29} NCs, respectively.

Fig. 6 The ns-TA kinetics of (A) free TMPyP, (B) TMPyP + Ag_{29} NCs (C) TMPyP + Au-doped Ag_{29} NCs in water after 650 nm laser excitation.

It is known that spin-orbit coupling facilitates ISC and triplet state formation. [42] As spin-orbit coupling is strongly proportional to the size/weight/charge of the nucleus, in this case, the heavy atom effect due to doping with Au atoms facilitates intersystem crossing and increases the triplet state population and consequently the triplet state lifetime.

4. Conclusion

In summary, a positively charged porphyrin shows strong ground- and excited-state interaction with Ag_{29} NCs, as evidenced by spectral changes in steady-state absorption, fluorescence, Raman and time-resolved experiments. The results indicate ultrafast electron injection from the porphyrin to undoped and Au-doped NCs, as shown by the formation of porphyrin radical cation within 300 fs. In this regime, we found that the positive charge on the meso unit of porphyrin and the negative charge of the surface of silver NCs is the key component and the main driving force for such interactions. In addition, our time-resolved data clearly demonstrate the possibility of modulating the CT and the triplet state population

of porphyrin on the NC surface by a metal doping effect. [43, 44] The novel insights reported in this work illuminate the key variable components not only for controlling the interfacial charge transfer but also for tuning the intersystem crossing and the triplet state lifetime at donor-acceptor interfaces.

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Highlights

- . An approach to tune the intersystem crossing and triplet state lifetime of porphyrin.
- . Ultrafast charge transfer at porphyrin-silver nanocluster interfaces.
- . Metalation-like structure of porphyrin cavity on the surface of silver nanoclusters.
- . Au doping can modulate the charge transfer and charge recombination of porphyrin on the surface of silver nanoclusters.

TOC graphic