In Search of Stable Visible Light Absorbing Photocatalysts: Gold Nanoclusters

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Abstract

Photochemical reactions are beginning to play an important role during the synthesis of complex organic molecules. The impetus to employ light initiated photoreactions as a synthetic tool derives from the fact these reactions require no reagents except light. Abundance of sunlight has prompted the chemists to search for visible light absorbing sensitizers (catalysts) to initiate the desired reactions. Our goal in this context is to develop stable and readily available catalysts that would function under sunlight. In this manuscript we present results of our experiments with gold nanoclusters (AuNCs) as a visible light absorbing catalysts. AuNCs absorb and emit in the visible region, soluble in water and transfers electron to suitable acceptors. Employing a series of acceptors we found that excited AuNC can transfer one electron to any acceptor whose reduction potential is above – 1.1 eV. In the excited state AuNC does not accept electrons. Also it did not serve as an energy transfer sensitizer even with molecular oxygen. We are optimistic that AuNP and AuNC could be developed into a stable and water-soluble visible light absorbing photocatalysts to perform useful photoreactions.

Key Words Nanoclusters, Photocatalysis, Electron transfer, Emission quenching, Visible light photocatalysis

Graphical Abstract

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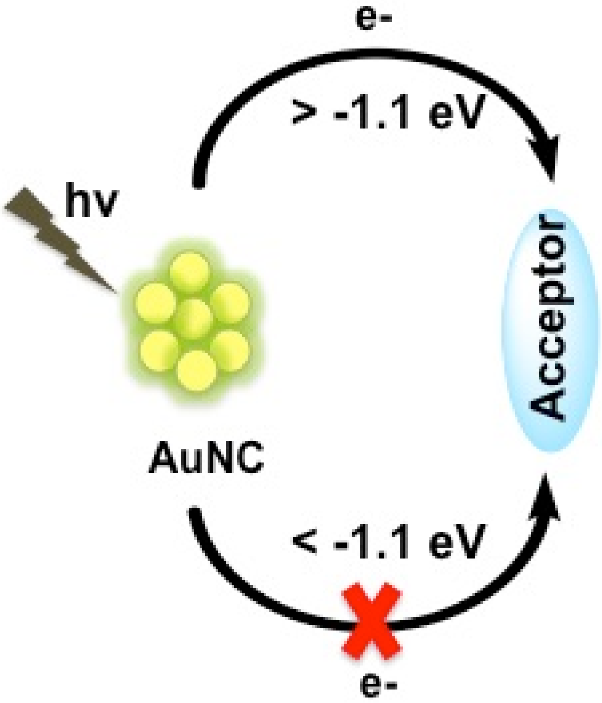
In the context of visible light photocatalysis gold nanoclusters upon light absorption were found to transfer electron to acceptors whose reduction potential is above –1.1 eV. AuNC has limited value as electron transfer sensitizers in photochemical reactions.



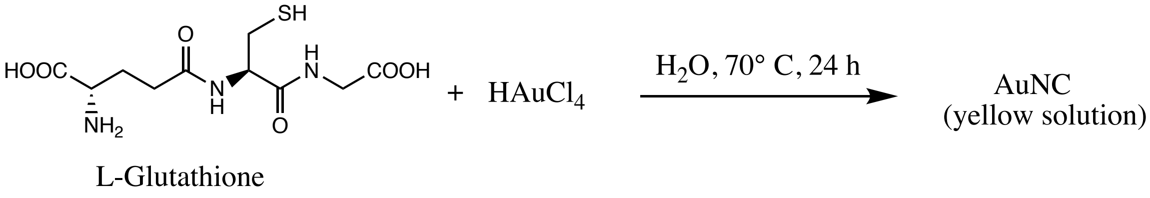
1. Introduction

Prompted by the need to carry out organic synthesis under 'green' and 'sustainable' conditions interest in visible light photocatalysis (VLPC) has grown during the last decade.[1-3] Energy and electron transfer concepts developed by pioneers during 1950-80 have been valuable for the development of this topic.[4] Among the VLPC enthusiasts, the term 'sensitizer' used in photochemical literature has taken a new label namely, 'catalyst'. Although numerous visible light absorbing organic dyes that could be used as catalysts (sensitizers) are available, their poor stability and tendency to aggregate have forced chemists to look for Ru, Re, Rb complexes and metal aggregates that absorb in the visible region as photocatalysts. In this context two types of metal nano aggregates with different properties have attracted attention. One is metal nanoparticles (NPs)[5-11] and the other is metal nanoclusters (NCs).[12-18] For example, metal nanoparticles of gold, silver and platinum are characterized by their distinct surface plasmon band in the visible spectrum extending to red while gold nanoclusters have a broad absorption in the visible region.[19] While metal nanoparticles are non-emissive, nanoclusters emit in the visible spectrum.[20-22] The nanoclusters are usually smaller in size than nanoparticles and their absorption and emission depend on their size and the stabilizing ligand. The properties of metal nanoclusters, in addition, depend on the method of preparation. The recent interest in this ultra small nanoclusters is due to their molecular like properties and emissive nature. The emissive property of these Au-thiolate clusters, their low toxicity, ultra small size, and good biocompatibility, make them ideal as bio imaging probes.

A recent report of an easy and reliable procedure to synthesize thiolate-protected water-soluble gold nanoclusters of 1-3 nm diameter.[23-24] prompted us to explore their use as visible light absorbing photocatalysts. Our interest in these systems stems from their possible use as energy and electron transfer sensitizers to initiate organic phototransformations.[25-29] With this in mind we have examined the electron and energy transfer properties of AuNC by quenching their emission with various organic molecules and oxygen. Our ultimate goal is to identify metal nanoclusters and nanoparticles that could act as an energy or electron transfer catalysts (sensitizers) in water.

2. Results and Discussion

Thiolate stabilized AuNC are commonly synthesized by reducing Au(I) thiolate complexes using reducing agent such as $NaBH_4$. These clusters show emission in the blue to near-IR region with low quantum yield. Recent research has established that slow decomposition of large Au-nanocrystals or Au-thiolate complex can also be used to synthesize AuNC. A facile one-pot synthesis of Au-thiolate has been reported recently by Xie and co-workers (**Scheme 1**). For the current investigation L-glutathione protected gold nanoclusters were synthesized using the method reported by Xie *et al.*[23-24] By this procedure, as the solution aged for 24 h, nanoclusters having a few-gold-atom core capped with Au(I) thiolate complex shell were formed. These AuNCs were characterized by their absorption, emission and ^1H NMR spectra, TGA and DLS data and TEM (**Figure S1-S5** in Supporting Information). These clusters absorb both in UV and visible region extending up to 500 nm. These AuNCs exhibited emission in the region 500-800 nm with maximum at 612 nm. The absorption and emission spectra of above synthesized Au nanoclusters are shown in **Figure 1**. These spectra are consistent with the ones reported in the literature. It is reported that these clusters consist of a mixture of different sizes consisting 29-43 Au atoms capped with glutathione molecules. The clusters prepared in this study we believe are a mixture and not a well-defined one with specific number of Au atoms. Having synthesized small AuNCs we were interested to examine whether these would act as electron and energy transfer sensitizers. Other workers have employed such types of clusters in the context of solar energy storage and water splitting.[30-31] However to our knowledge these have not been used as sensitizers in organic photochemistry. The emissive nature distinguishes these clusters from larger nanoparticles that have characteristic plasmonic properties and do not emit.



Scheme 1. Method used to synthesize Au-glutathione nanocluster (AuNC)

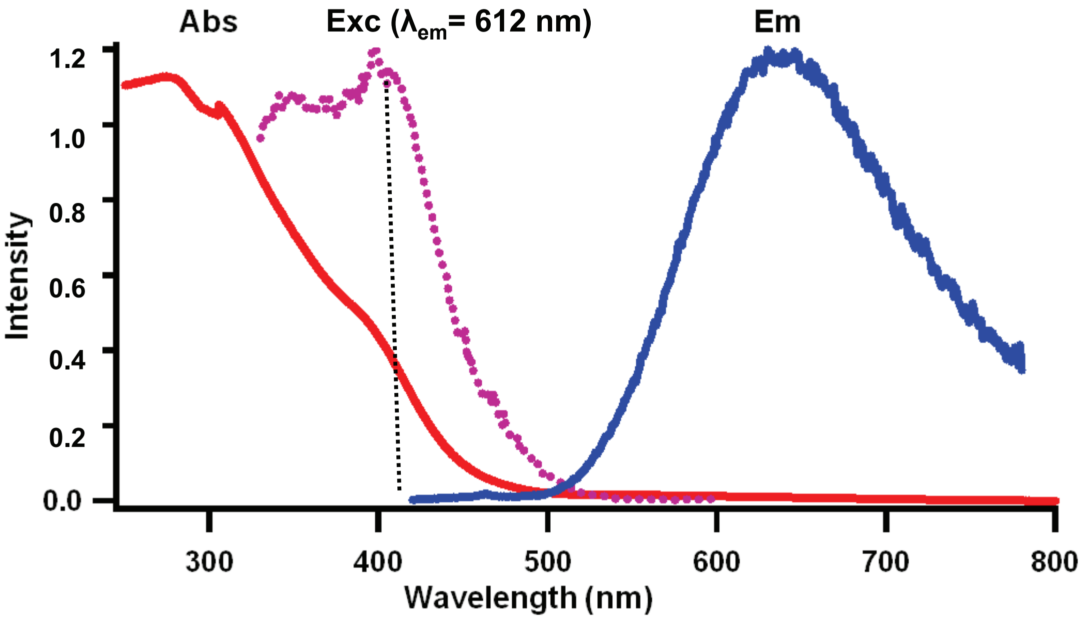
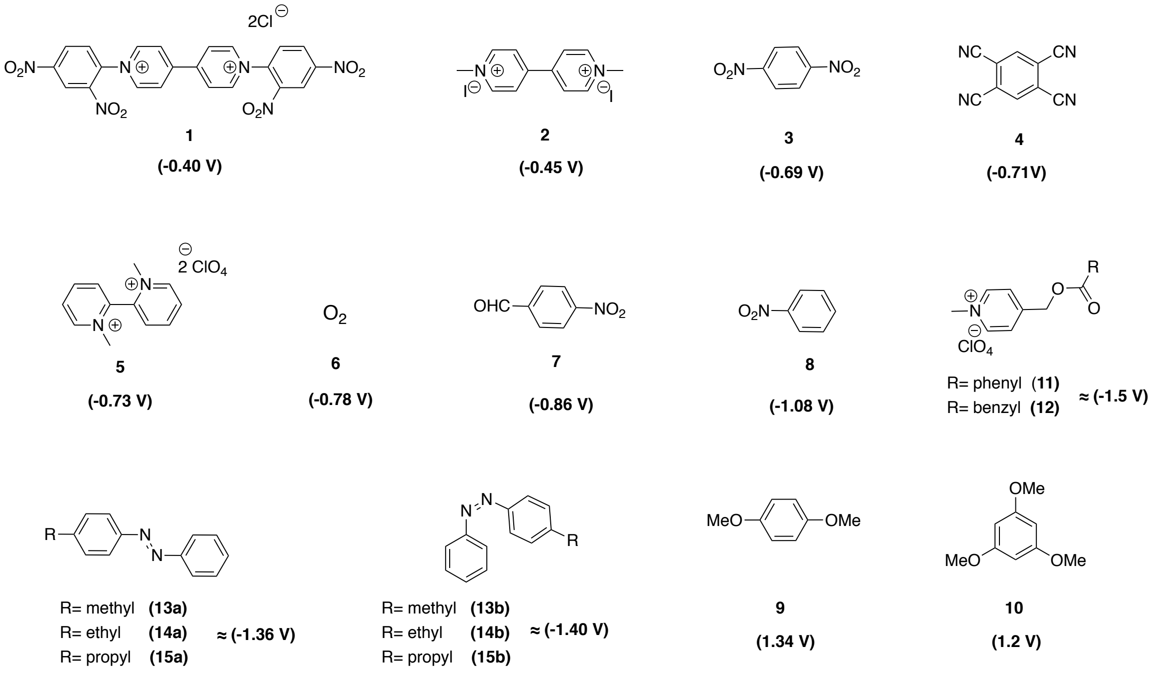


Figure 1. Normalized absorbance (red line), excitation (pink line) monitored at 612 nm and emission spectra (blue line, λ_{ex} = 400nm) of AuNC.

With our interest to examine whether these clusters could act as good electron transfer agents, we conducted fluorescence quenching experiments with various organic electron acceptors and donors. The quenchers examined and their redox potential data are listed in **Scheme 2**. Electron transfer properties of these clusters were probed by recording fluorescence and measuring the excited state lifetime in presence of quenchers. Cluster emission was quenched by methyl viologen (**2**) and its derivative (**1**). Stern-Volmer plots of quenching by **1** and **2** shown in **Figures 2** and **3** indicate that the I_0/I and τ_0/τ do not overlap. Since there are changes in lifetimes the quenching is not completely by a static process. If this is truly a static process the donor (AuNC) and the acceptor (viologens) should be in physical contact prior to excitation. We were curious to know whether the viologen that is included within a cucurbiturils (CB) would be able to establish contact and quench the AuNC emission. As illustrated in **Figure 4**, CB[7] included **2** (i.e., **(2@CB[7])** failed to quench the cluster emission. This suggested that AuNC and the electron acceptor have to be in physical contact for electron transfer to occur. Whether it is static or dynamic the electron transfer is prohibited by the walls of the host CB[7]. Due to lack of time resolved transient absorption facilities we did not measure the rate of electron transfer. However, the recent report by Kamat's group indicated that AuNC is quenched by **2** at > 5×10^{10} $M^{-1} s^{-1}$ that is higher than the rate of diffusion.[28] This is consistent with our conclusion of the quenching proceeding by a static process. Since the excited state energies of **1** and **2** are expected to be above that of AuNC we believe that the process by which the quenching occurs is via electron transfer.



Scheme 2. Structures of molecules used as acceptors and donors. Redox potentials reported are with respect to SCE in CH_3CN except in **1** where it is with respect to SCE in DMF. Reduction potentials of **1-8** and **11-15** and oxidation potentials of **9** and **10** are provided in parenthesis.

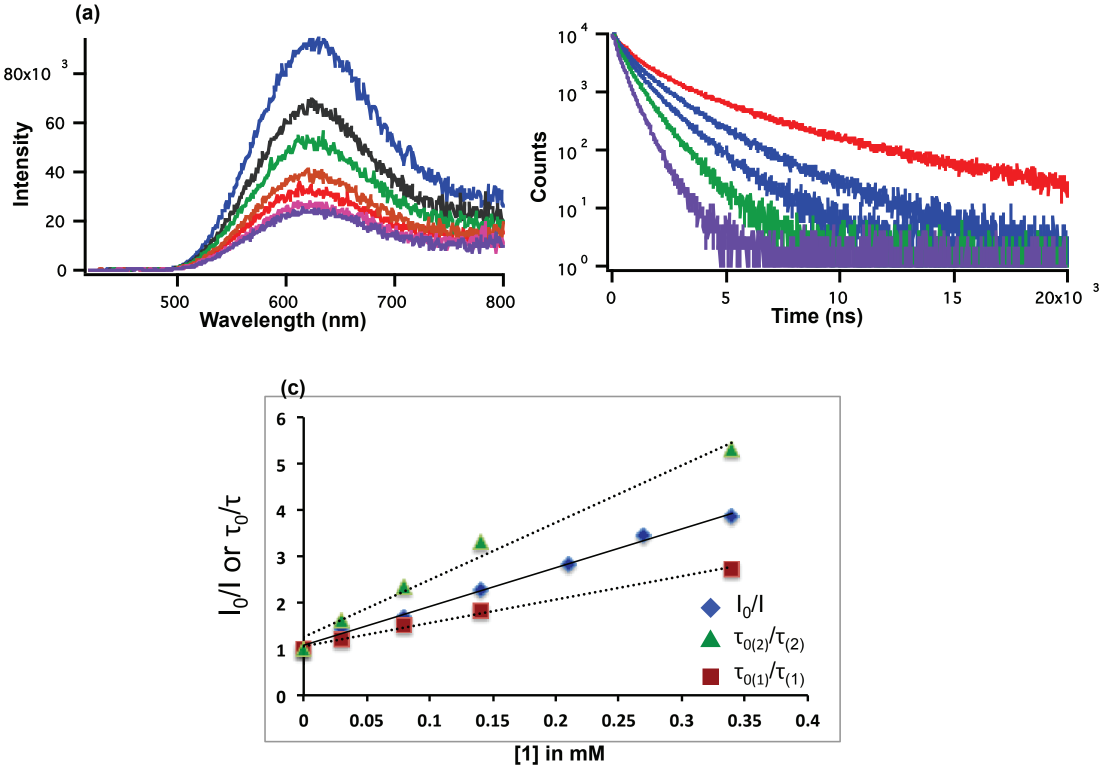


Figure 2. Quenching of emission of AuNC by **1** in H_2O (a) Emission spectra (b) Lifetime measurements (c) Stern-Volmer plot for emission and lifetime. λ_{ex}=400 nm, λ_{em}= 600 nm, [AuNC]= 10^{-4} M; [**1**] = 0 to 3.4×10^{-3} M. The excited AuNC decayed via two exponentials and both are plotted in (c).

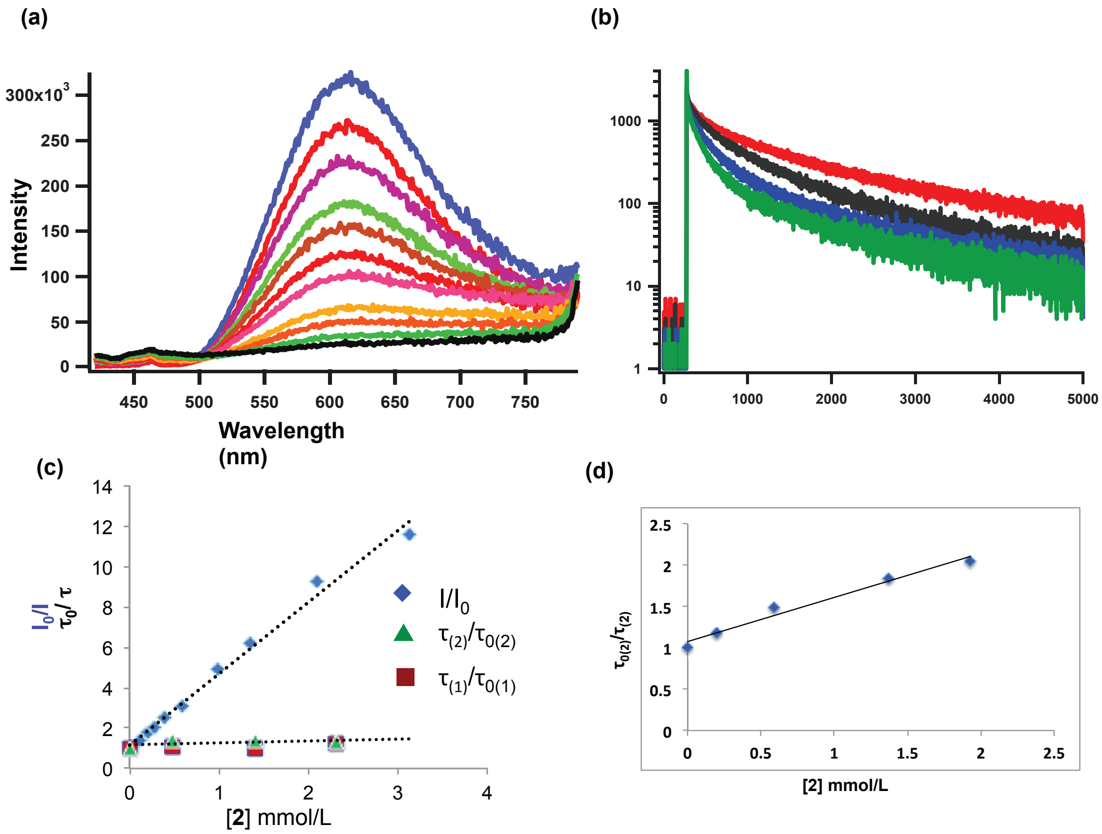


Figure 3. Quenching of emission of AuNC by **2** in H_2O (a) Emission spectra (b) Lifetime measurements (c) Stern-Volmer plot for emission and lifetime. λex=400 nm, λem= 600 nm, [AuNC]= 10^{-4} M; [**2**] = 0 to 3.1×10^{-3} M. The AuNC decayed via two exponentials and both are plotted in (c). Figure (d) provides Stern-Volmer plot for the faster component of the decay.

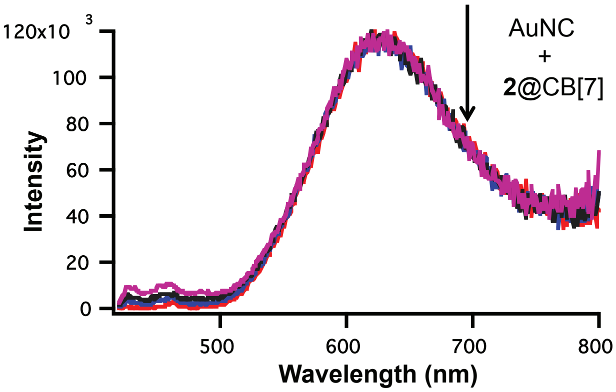


Figure 4. Emission spectra of AuNC upon addition on **2**@CB[7] (CB[7] methyl viologen complex). , [AuNC]= 10^{-4} M; [**2**@CB[7]] = 0 to 2×10^{-4} M

To probe whether AuNC would also act as an energy transfer sensitizer we chose oxygen as the acceptor. We believed that oxygen with excited singlet energy of 22 kcal/mol would be an ideal acceptor for energy transfer from excited AuNC. As illustrated in **Figure 5** molecular oxygen quenched the emission of AuNC. Quenching of AuNC emission by O_2 was studied in three different solvents, H_2O, dimethyl sulfoxide and methanol. Since the solubility of oxygen differed in these solvents, we expected the rate of quenching would vary. In methanol where the O_2 dissolves better than in the other two solvents the cluster emission was quenched more efficiently than in H_2O and DMSO (**Figure S10-S11**). If the quenching is due to energy transfer singlet oxygen should be generated in solution. Singlet oxygen in principle can occur from either excited singlet (when the S_1–T_1 gap is more than 22 kcal/mol) or from triplet when it is above 22 kcal/mol. However characteristic singlet oxygen emission (1268 nm) was not detected when an oxygen saturated solution of AuNC was excited at 400 nm (**Figure 6**). This suggested that energy transfer is not the process by which oxygen quenches the AuNC emission. However, generation of singlet oxygen from well-defined $Au_{25}(SR)_{18}$ cluster has been reported in the literature.[32] The fact that the emission of AuNC is quenched by oxygen suggested that most likely it occurs by electron transfer. Our attempts to detect the product of electron transfer namely superoxide anion were not successful.

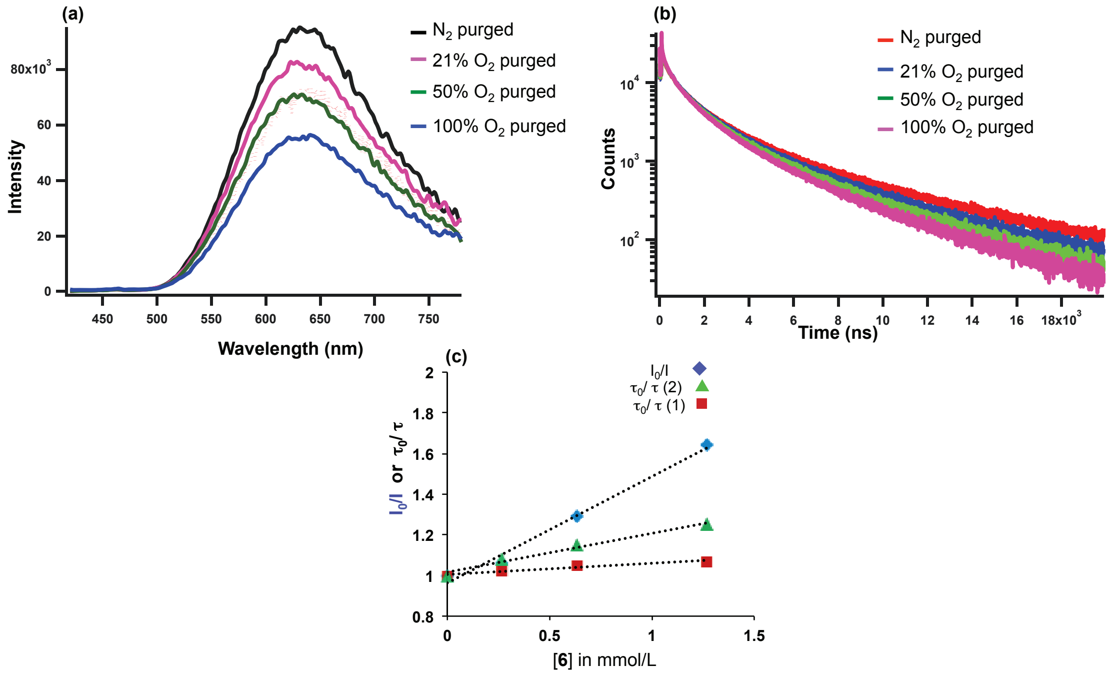


Figure 5. Quenching of emission of AuNC by oxygen in H_2O (a) Emission spectra (b) Lifetime measurements (c) Stern-Volmer plot for emission and lifetime. λ_{ex}=400 nm, λ_{em}= 600 nm, [AuNC]= 10^{-4} M. Solution was purged with oxygen-nitrogen mixture; the percentage of oxygen is indicated above. The AuNC decayed via two exponentials and both are plotted in (c).

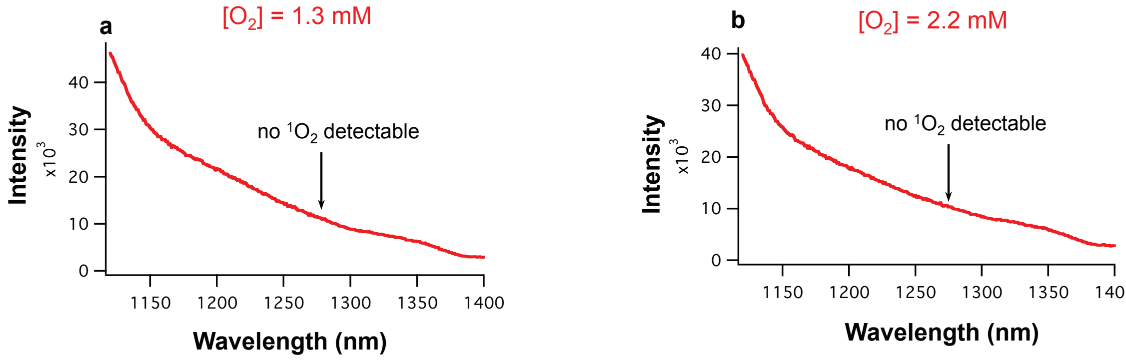


Figure 6. Emission spectra of AuNC solution saturated with oxygen (a) D_2O and (b) DMSO-d_6. λ_{ex}: 400 nm.

Ability of oxygen to quench AuNC emission suggested that it could oxidize systems with reduction potential of at least – 0.78 eV. To determine the oxidation power of the AuNC we used several quenchers with reduction potentials varying between – 0.40 and – 1.5 eV. The list of quenchers included 2, 4 dinitro phenol (**3**), 1, 2, 4, 5-tetracyano benzene (**4**), 2, 2'-bipyridinium N, N' dimethyl (**5**), 4-nitro benzaldehyde (**7**), and nitro benzene (**8**). Their structure and reduction potentials are provided in **Scheme 2**. Stern-Volmer plots for quenching by these acceptors are shown in **Figure 7**. Individual emission and lifetime quenching spectra and traces are provided in SI (**Figure S6-S9**). Although nitrobenzene quenched the emission, the pyridinium derivatives **11** and **12** did not. This suggested that the limitation of AuNC to reduce organic molecules resided some where in between – 1.0 eV and –1.5 eV. Based on the results shown in **Figure 7** we believe that AuNC can reduce organic molecules whose potential is above – 1.1 eV. The fact that nitrobenzaldehyde but not nitrobenzene quenches the AuNC emission is a clear indication of the limitation of excited AuNC as a reductant. AuNP often act both as an oxidant and reductant.[33-35] To probe whether AuNC has similar property we used di- and trimethoxy- benzenes as electron donors (**Scheme 2**). As illustrated in **Figure 8** no quenching was observed even with a good electron donor such as 1, 3, 5-trimethoxy benzene.

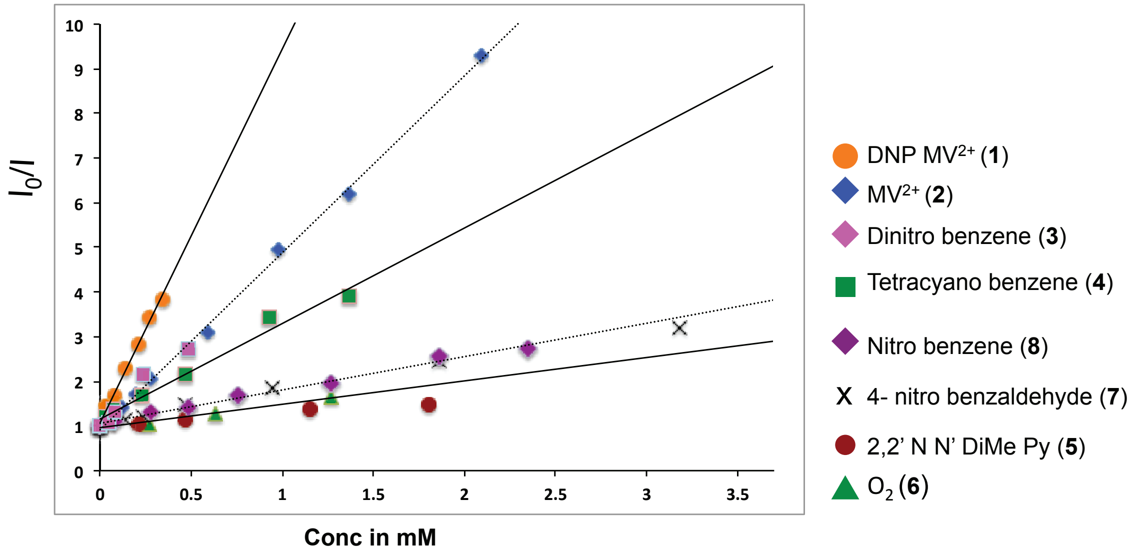


Figure 7. Stern-Volmer plot for fluorescence quenching experiment with various acceptors.

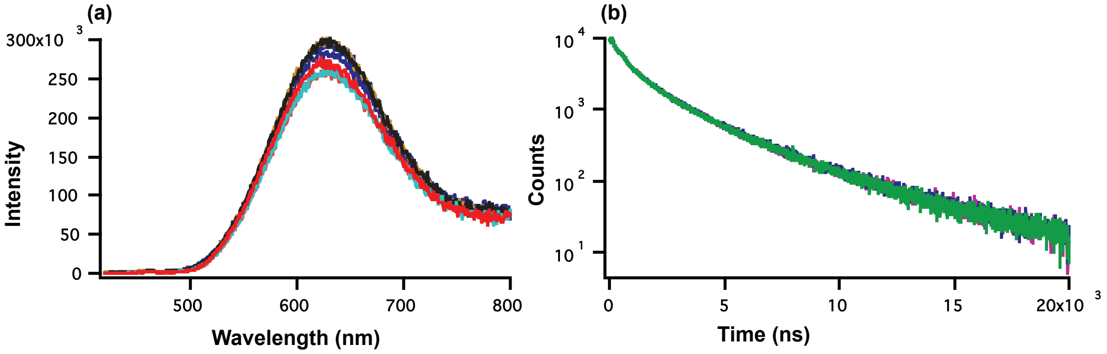
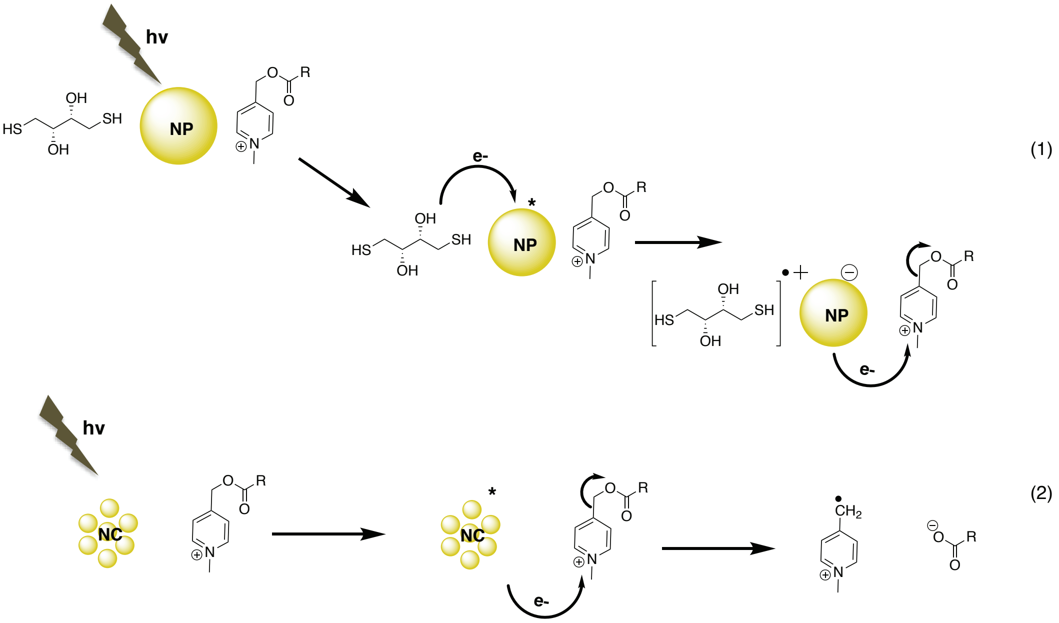


Figure 8. AuNC emission in presence of 1,3,5-trimethoxy benzene in H_2O (a) Emission spectra (b) Lifetime measurements. λ_{ex}=400 nm, λ_{em}= 600 nm, [Au NCs]= 10^{-4} M [**10**] = 0 to 2.0×10^{-3} M.

Thus the results with the electron donors and acceptors listed in **Scheme 2** lead us to conclude that the AuNC is an electron donor and not an electron acceptor. Also results with oxygen suggested that AuNC is not an energy donor. As mentioned in the introduction section, desire to identify visible light absorbing light-stable sensitizers drew our attention to gold nanoparticles and clusters. In this context we were particularly attracted by the studies of Falvey's group in which they demonstrated that carboxylic acids could be released by a phototriggering reaction initiated by AuNP through an electron transfer process (**Scheme 3**, **eq**. **1**).[36] In their studies dithiothreitol served as the primary electron donor to excited AuNP. We experimented the same reaction with AuNC without an additional electron donor (**Scheme 3**, **eq**. **2**). As shown in **Figure 9**, as expected based on reduction potential, AuNC emission was not significantly quenched by the photoprotected esters **11** and **12**. Given that AuNC is able to reduce substrates having reduction potentials only above – 1.1 eV, the inability of the two esters (– 1.5 eV) to quench was not surprising. As expected, irradiation of a solution of AuNC and the two esters did not result in any reaction. We plan to pursue this study employing more easily reducible triggers such as methylviolgen etc. and in presence of an additional electron donor.



Scheme 3. (Top): Steps during decarboxylation of N-methylpicolinium ester triggered by visible light absorbing AuNP. (Below) Visualized steps during decarboxylation of N-methylpicolinium ester triggered by visible light absorbing AuNC

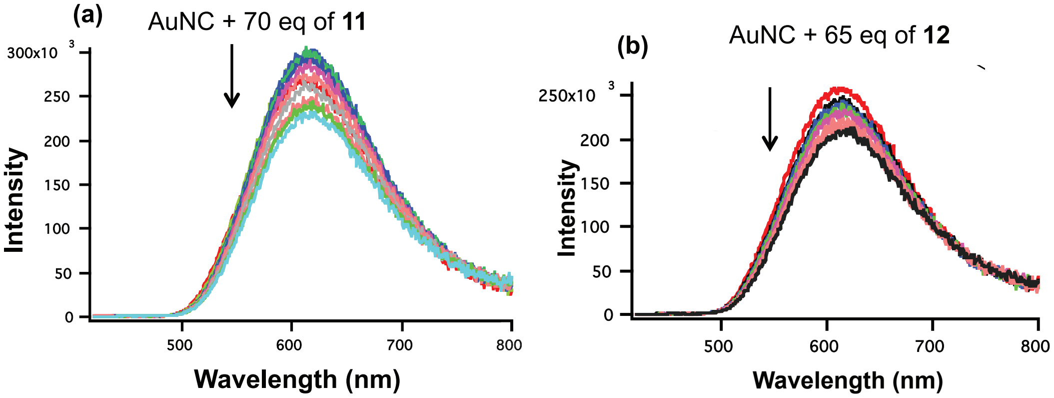
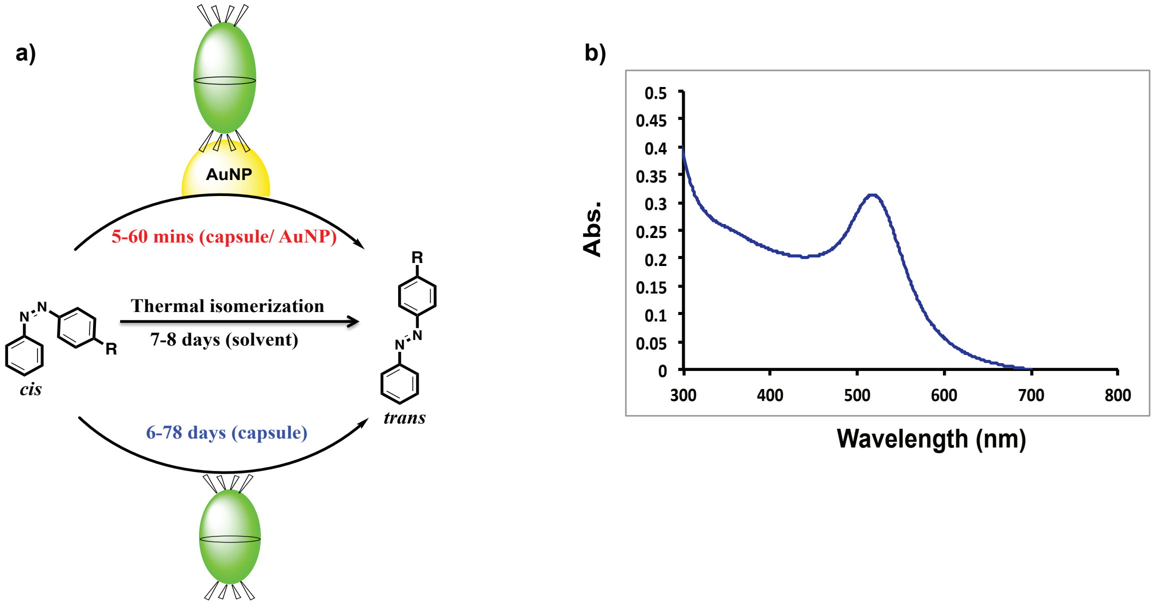


Figure 9. Fluorescence quenching of AuNC by N-methylpicolinium esters in methanol, (a) using **11** and (b) **12**. Quenching in both cases were minimal.

One other reaction that worked best with AuNP was the thermal isomerization of *cis*- to *trans*-azobenzene.[37] The process is illustrated in **Scheme 4**. *cis*-Azobenzene prepared photochemically from *trans*-azobenzene slowly reversed to the trans isomer in a week (Figure S15a). However, when it is included within an organic capsule (octa acid) it took over two months (Figure S15b). However, most interestingly when the capsule containing *cis*-azobenzene was stirred with AuNP the isomerization occurred within an hour (**Figure S15c**). Clearly the AuNP hastened the isomerization, presumably through an electron transfer process from AuNP to the ground state *cis*-azobenzene. We wished to probe whether AuNC will do the same. With this in mind *cis*-azobenzene encapsulated octa acid capsule was stirred with AuNC in water for several hours. There was no conversion of *cis* to *trans* in presence of AuNC. From this result it is clear that AuNC behaves distinctly differently from AuNP. To test whether excited AuNC will initiate isomerization by transferring an electron to octa acid encapsulated *cis*-azobenzene we performed AuNC emission quenching experiments. As shown in **Figure 10** addition of octa acid encapsulated *cis*-azobenzene or *trans*-azobenzene did not result in quenching of AuNC emission. Clearly AuNC even from the excited state do not initiate the isomerization of azobenzenes. This is consistent with the results with several quenchers (**Scheme 2**) discussed above. The reduction potential of azobenzenes (~ – 1.4 eV) are too low for AuNC to reduce them and initiate isomerization.



Scheme 4. (a) Environment dependent isomerization of *cis*-azobenzene. (b) Absorption spectrum of AuNP used in the study.

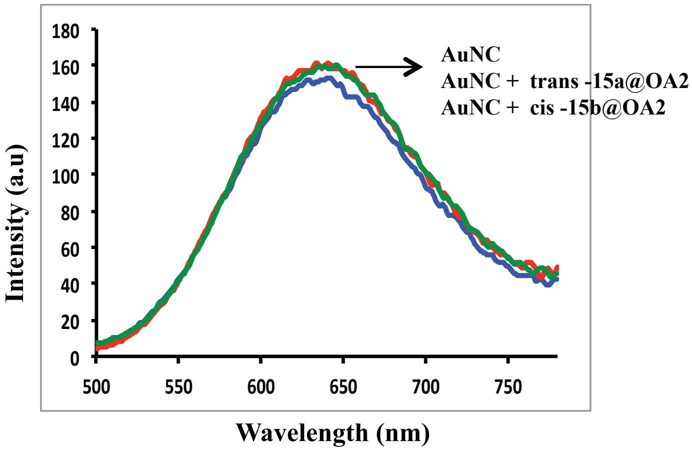


Figure 10. Emission spectra of AuNC solution after addition of both *cis* and *trans* isomer of **15**@OA$_2$

Conclusions

Our recent interest in visible light photocatalysis prompted us to identify stable molecules/materials that would absorb in the visible spectrum and function as sensitizers and initiate transformations of organic molecules by transferring either energy and/or electron.[38-41] This led us to stable and clean gold nanoparticles and nanoclusters. These well-explored materials have absorptions in the visible spectrum and act as electron and energy transfer agents. In spite of their dominance in materials science, to our knowledge they have not been commonly used as sensitizers to initiate organic photoreactions. Thanks to the report by Xie,[23-24] AuNC that absorbs in the visible region can be easily synthesized. AuNC thus synthesized consists of a mixture of clusters of different sizes. The above AuNC has limited ability to serve as electron donor. It can reduce organic molecules whose reduction potentials are above ~ – 1.1 eV. Based on the fluorescence quenching experiments we believe that AuNC has only limited ability to serve as energy transfer sensitizer. It is quite likely that well defined AuNC such as Au$_{25}$NC will have better ability to reduce wide ranging substrates and would serve as energy transfer sensitizers. We plan to continue our search for stable visible light absorbing sensitizers (catalysts) that would find use in the current burgeoning field of VLPC.

Acknowledgement

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Supplementary Information (SI)

All experimental details that include synthesis and characterization of AuNC, procedures for recording emission and lifetime and quenching of emission and lifetime are provided as Supporting Information.

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