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Synthesis and Photodynamics of 9-Mesitylacridinium Ion-Modified Gold Nanoclusters

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Abstract: Photoexcitation of gold nanoclusters covalently functionalized with 9-mesityl-10-methylacridinium ion (Mes-Acr$^+$) resulted in the formation of the electron-transfer state (Mes$^{\bullet+}$-Acr$^\bullet$), which forms a π-dimer radical cation with the neighboring Mes-Acr$^+$ via an intramolecular $\pi-\pi$ interaction.

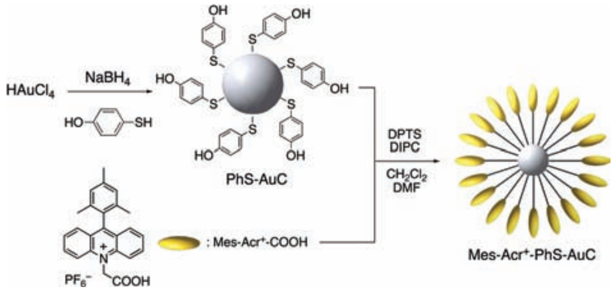
Alkanethiolate-monolayer-protected metal nanoclusters (MPCs), which can provide three-dimensional (3D) architectures, have attracted much attention because they are stable in air and soluble in both nonpolar and polar organic solvents, allowing their facile modification with other functional thiols through exchange reactions or by couplings and nucleophilic substitutions.[1−3] Thus, MPCs have been modified with a variety of functional molecules.[4−9] Among them, construction of the 3D architectures of porphyrin MPCs has merited special interest because of the improved light-harvesting efficiency.[4,10,11] Porphyrin MPCs can form π complexes with C_{60}, which have been utilized to construct supramolecular solar cells.[12] Extensive efforts have to date been devoted to the design and synthesis of electron donor−acceptor ensembles to mimic the charge-separation process in the photosynthetic reaction center.[13] However, assembly of such donor−acceptor ensembles on MPCs has yet to be explored.

We report herein the synthesis and photodynamics of 9-mesitylacridinium ion-monolayer-protected gold nanoclusters (Mes-Acr$^+$-PhS-AuC). The 9-mesitylacridinium ion (Mes-Acr$^+$) is an electron donor−acceptor dyad in which the electron-donor (mesityl) moiety is directly connected to the acceptor (acridinium ion) moiety.[14] The comparison of the photodynamics of Mes-Acr$^+$-PhS-AuC with the reference compound without gold nanoclusters provides an excellent opportunity to clarify how assembly of the electron donor−acceptor dyad on MPCs affects the photoinduced electron-transfer (ET) process.

Mes-Acr$^+$-PhS-AuC was prepared by the coupling between the functional molecules and Au nanoclusters [see the Experimental Section in the Supporting Information (SI)]. Carboxyl-terminated Mes-Acr$^+$-COOH[15] was directly coupled to 4-mercaptophenol-functionalized Au nanoclusters (PhS-AuC) in the presence of *N*,*N*′-diisopropylcarbodiimide (DIPC) and 4-(*N*,*N*-dimethylamino)pyridinium-4-toluenesulfonate (DPTS) as the standard coupling agents, as shown in Scheme 1.[16] The reference compound (Mes-Acr$^+$-COOPh) was prepared by condensation of Mes-Acr$^+$-COOH and phenol (see the SI).

The UV−vis spectrum of Mes-Acr$^+$-PhS-AuC exhibited absorption bands at 360 and 420 nm due to Mes-Acr$^+$, as did the spectrum of Mes-Acr$^+$-COOPh (Figure S1 in the SI). This suggests that there is no significant interaction between Mes-Acr$^+$ molecules on AuC. The mean diameter of the Au core was determined to be 1.7 ± 0.3 nm by transmission electron microscopy (TEM) (Figure 1). The ^{1}H NMR spectrum of Mes-Acr$^+$-PhS-AuC was measured in DMSO-d_6 containing 1,4-dioxane (1.0 mM) as an internal standard (Figure S2). The signal peak derived from the Mes-Acr$^+$ moiety was observed at 6.5−9.0 ppm. The amount of Mes-Acr$^+$ was determined to be 58 molecules per AuC (75% coverage) on the basis of integration of the ^{1}H NMR signals due to the Mes-Acr$^+$ moiety. From the distance between two Au atoms (4.06 Å) in the crystal lattice of Au, the distance between two neighboring Mes-Acr$^+$ molecules on the Au surface was estimated to be 8.3 Å (Figure S3). Thus, Mes-Acr$^+$ molecules are closely assembled on AuC.

Scheme 1



Femtosecond transient absorption spectroscopy of Mes-Acr$^+$-PhS-AuC with excitation at 420 nm revealed a transient absorption band at 490 nm and a broad transient absorption band in the near-IR (NIR) region, as shown in Figure 2a. The broad NIR band is assigned to the π-dimer radical cation formed from the ET state of Mes-Acr$^+$ (Mes$^{\bullet+}$-Acr$^\bullet$-PhS-AuC) and the neighboring Mes-Acr$^+$.[17,18] This indicates that the close proximity of Mes-Acr$^+$ molecules on AuC makes it possible to form the π-dimer radical cation via an intramolecular $\pi-\pi$ interaction upon photoinduced ET from the Mes moiety to the singlet excited state of the Acr$^+$ moiety. In the case of the reference compound (Mes-Acr$^+$-COOPh), the transient absorption band at 490 nm due to the ET state of Mes-Acr$^+$-COOPh (Mes$^{\bullet+}$-Acr$^\bullet$-COOPh) was observed at 10 ps, but there was no transient absorption band in the NIR region,

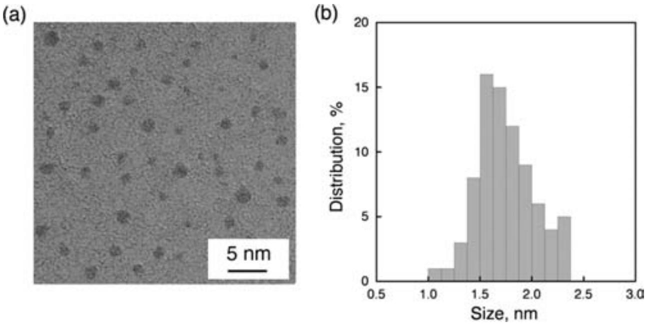


Figure 1. (a) TEM image and (b) core size histogram of Mes-Acr$^+$-PhS-AuC.

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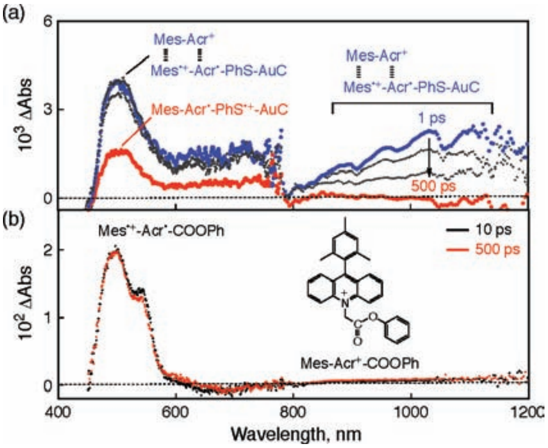
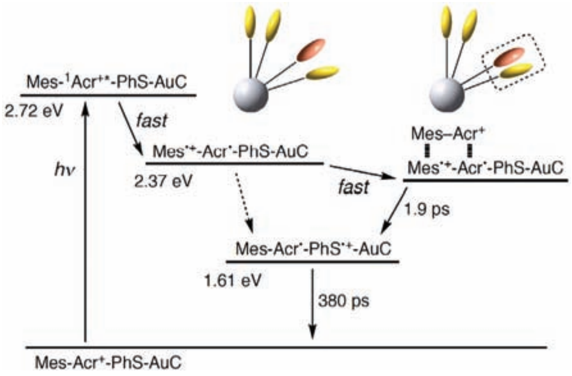


Figure 2. Transient absorption spectra observed in femtosecond laser flash photolysis ($\lambda_{ex} = 420$ nm) of (a) Mes-Acr$^+$-PhS-AuC at 1 and 500 ps and (b) Mes-Acr$^+$-COOPh at 10 and 500 ps in MeCN at 298 K.

Scheme 2



as shown in Figure 2b. However, the broad NIR band appeared at 10 μs in nanosecond laser flash photolysis (Figure S4). This indicates that the π-dimer radical cation of Mes$^{\bullet+}$-Acr$^{\bullet}$-COOPh with Mes-Acr$^+$-COOPh was formed by the intermolecular reaction, in sharp contrast to intramolecular formation of the π-dimer radical cation at 1 ps in Figure 2.[17a]

The decay time profiles at 490 and 1020 nm due to the π-dimer radical cation of Mes$^{\bullet+}$-Acr$^{\bullet}$-PhS-AuC exhibited monoexponential decays with different lifetimes (1.9 ps at 1020 nm and 380 ps at 490 nm; Figure S5a), whereas the ET state of the reference compound (Mes$^{\bullet+}$-Acr$^{\bullet}$-COOPh) exhibited no decay in this range (Figure S5b). The faster decay at 1020 nm is ascribed to ET from the benzenethiol group (PhS) to the Mes$^{\bullet+}$ moiety of the π-dimer radical cation of Mes$^{\bullet+}$-Acr$^{\bullet}$-PhS-AuC to produce Mes-Acr$^{\bullet}$-PhS$^{\bullet+}$-AuC, which still has the absorption at 490 nm. Such a charge shift occurs because the one-electron oxidation potential (E_{ox}) of the PhS moiety, which was determined to be 1.12 V vs SCE (Figure S6), is significantly lower than the one-electron reduction potential of the Mes$^{\bullet+}$ moiety of the ET state ($E_{red} = 1.88$ V vs SCE).[14] The resulting ET state (Mes-Acr$^{\bullet}$-PhS$^{\bullet+}$-AuC) decays with a lifetime of 380 ps, whereas Mes$^{\bullet+}$-Acr$^{\bullet}$-COOPh exhibits little decay, because the driving force of back-ET in Mes-Acr$^{\bullet}$-PhS$^{\bullet+}$-AuC (1.61 eV) is significantly smaller than that in Mes$^{\bullet+}$-Acr$^{\bullet}$-COOPh (2.37 eV) in the Marcus inverted region.

The energy diagram of the photoinduced ET in Mes-Acr$^+$-PhS-AuC is summarized in Scheme 2. Photoexcitation of Mes-Acr$^+$-PhS-AuC at 420 nm affords the singlet excited state of the Acr$^+$ moiety (Mes-^{1}Acr^{+*}), and this is followed by rapid intramolecular ET from the Mes moiety to the ^{1}Acr^{+*} moiety accompanied by formation of the π-dimer radical cation between the ET state and the neighboring Mes-Acr$^+$ on AuC. The π-dimer radical cation decays with a lifetime of 1.9 ps by ET from the benzenethiol linker to the π-dimer radical cation (Mes$^{\bullet+}$-Mes) moiety and back-ET to the ground state with a lifetime of 380 ps.[19]

In conclusion, photoexcitation of gold nanoclusters (AuC) functionalized with Mes-Acr$^+$ results in rapid formation of the ET state (Mes$^{\bullet+}$-Acr$^{\bullet}$), which forms a π-dimer radical cation with the neighboring Mes-Acr$^+$ on AuC, whereas such π-dimer radical cation formation occurs on a much longer time scale for the reference compound (Mes-Acr$^+$-COOPh) by the intermolecular reaction between Mes$^{\bullet+}$-Acr$^{\bullet}$-COOPh and Mes-Acr$^+$-COOPh. Thus, it has been demonstrated for the first time that the assembly of electron donor−acceptor molecules on AuC results in efficient photoinduced ET to form the π-dimer radical cation, in contrast to the case in solution.

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Supporting Information Available: Experimental procedures and Figures S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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