JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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Real-Time Observation of Tight Au−Au Bond Formation and Relevant Coherent Motion upon Photoexcitation of $[Au(CN)_2^-]$ Oligomers

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Supporting Information

ABSTRACT: Structural dynamics involving tight Au−Au bond formation of excited-state oligomers $[Au(CN)_2^-]_n$ was studied using picosecond/femtosecond time-resolved emission and absorption spectroscopy. With selective excitation of the trimer ($[Au(CN)_2^-]_3$) in aqueous solutions, transient absorption due to the excited-state trimer was observed around 600 nm. This transient exhibited a significant intensity increase ($\tau = 2.1$ ps) with a blue shift in the early picosecond time region. Density functional theory (DFT) and time-dependent DFT calculations revealed that the observed spectral changes can be ascribed to a structural change from a bent to a linear staggered structure in the triplet excited-state trimer. The transient absorption also exhibited a clear modulation of the peak position, reflecting coherent nuclear wave packet motion induced by photoexcitation. The frequencies of the coherent motions are 66 and 87 cm^{-1}, in very good accord with the frequencies of two Au−Au stretch vibrations in the excited state of the trimer calculated by DFT. Time-resolved emission spectra in the subnanosecond time region showed that association of the excited-state trimer with the ground-state monomer proceeds with $\tau = 2.0$ ns, yielding the excited-state tetramer.

Gold(I) complexes have attracted much attention in the field of photophysics and photochemistry of metal complexes.[1−5] One of the most conspicuous features of gold(I) complexes is self-assembly due to the aurophilic interaction.[6,7] This interaction causes an attractive force between closed-shell Au(I) ions that can be as strong as hydrogen bonding.[8] The Au−Au bonding becomes distinctly strong in the electronically excited state, as an electron in a $d_{z^2}\sigma^*$ antibonding orbital is excited to a $p_z\sigma$ bonding orbital between the Au atoms (Figure 1).[7,9,10] As a result, gold(I) complexes often exhibit characteristic emission arising from the Au−Au bonding.[2,5] Investigation of the excited-state Au−Au interactions and related phenomena is indispensable for understanding of photochemistry of gold(I) complexes.[3,8]

Oligomers of the simplest gold(I) complex, dicyanoaurate ($[Au(CN)_2^-]$), show spectroscopic properties that directly reflect self-assembly in solution.[6,7,10−12] Recently, Patterson and co-workers reported that $[Au(CN)_2^-]_n$ oligomers exhibit phosphorescence in the 300−500 nm region upon photoexcitation of the $p_z\sigma \leftarrow d_{z^2}\sigma^*$ transition. The emission peak was found to be strongly dependent on the concentration of the Au(I) complex, which they called "exciplex tuning".[13−16] This change in phosphorescence has been explained in terms of the change in the size of the Au(I) oligomers. On the basis of quantum-chemical calculations at the MP2 level, the emission bands at ∼280 and ∼390 nm were assigned to an excited-state dimer and an excited-state trimer having a staggered structure, respectively. The band appearing at 420−470 nm was attributed to more aggregated excited-state oligomers.[7]

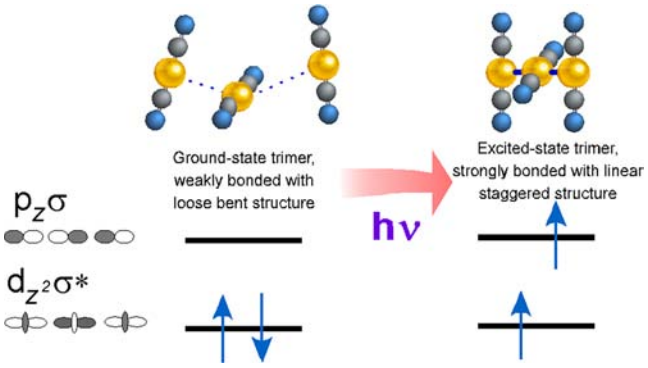


Figure 1. Frontier orbitals involved in the photoexcitation of $[Au(CN)_2^-]_3$ oligomer.

Although these exciplex-tuning systems have been studied in detail in the fluid and solid phases with steady-state spectroscopy,[13−22] knowledge about the structural dynamics is still lacking. Quantum-chemical calculations indicated that the most stable geometry of the oligomers $[Au(CN)_2^-]_n$ (n = 2,3) is a linear staggered structure in the T_1 state.[7] On the other hand, the oligomers have loose bent structures in the S_0 state because of the relatively weak Au−Au bonds (Figure 1). It was estimated that the Au−Au bonding energy in the T_1 state (∼1 eV)[7] is much higher than that in the S_0 state (∼0.1 eV),[6] which causes a substantial difference in not only the Au−Au distance (d_{Au-Au}) but also the rigidity of the structure. Therefore, photoexcitation of metallophilic oligomers is expected to induce a drastic structural change in the excited state. However, direct observation of the structural dynamics of $[Au(CN)_2^-]_n$ has not been reported, and no experimental evidence for the

Received: October 10, 2012
Published: December 31, 2012

dx.doi.org/10.1021/ja310004z | *J. Am. Chem. Soc.* 2013, 135, 538−541

tightening and/or shortening of the Au–Au bonding has been obtained in fluid media. Recently, advanced time-resolved spectroscopy enabled us to unveil the ultrafast dynamics of metal complexes and to observe coherent nuclear wave packet motions in not only the initial photogenerated state[23] but also the relaxed state after intersystem crossing (ISC)[24,25] and metal–metal bond tightening.[26,27] Here we report a time-resolved emission and absorption study of $[Au(CN)_2^-]_3$ over a wide time range from femtoseconds to nanoseconds. We clearly observed spectral changes due to the rapid structural dynamics in the excited state and detected photoinduced coherent Au–Au stretching motions induced by the formation of strong *intermolecular* Au–Au bonds.

An aqueous solution of $[Au(CN)_2^-]$ shows absorption in the UV region, and its red edge is shifted more to the red with increasing concentration [Figure S1 in the Supporting Information (SI)]. We examined the equilibrium among different oligomers and their extinction coefficients, and found that the absorption of a ~0.3 mol/dm^3 solution at 310 nm is dominated by the trimer, $[Au(CN)_2^-]_3$ (see section 2 in the SI). We selectively photoexcited the trimer in solution at 310 nm and examined its dynamics.

Figure 2 shows time-resolved emission spectra recorded with a streak camera after photoexcitation of a $K[Au(CN)_2]$ aqueous solution (0.27 mol/dm^3). Immediately after photoexcitation, an intense emission band with $\lambda_{max} < 400$ nm was observed. Although its lifetime was shorter than the response of the streak camera (~20 ps), we determined it to be ~0.5 ps by fluorescence upconversion (Figure S2). This short-lived emission is assignable to the fluorescence from the excited trimer. In the spectrum at 0.4 ns, a relatively weak emission was seen around 400 nm (black curve in Figure 2). According to Patterson, this weak emission is due to the phosphorescence of the excited-state trimer with a staggered structure.[7] As the phosphorescence of the trimer decayed with a time constant of 2.0 ns, a new emission appeared around 460 nm. The time constant of 2.0 ns is close to that calculated for a diffusion-controlled association between the trimer and a monomer (1.2 ns in H_2O; see the SI for details). Thus, the 460 nm emission, which decayed with a lifetime of 13 ns, is attributed to the phosphorescence of larger excited-state oligomers (e.g., the excited-state tetramer), which is also consistent with Patterson's assignment.

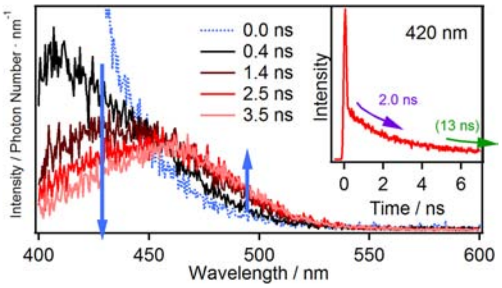


Figure 2. Picosecond time-resolved emission spectra of an aqueous solution of $K[Au(CN)_2]$ (0.27 mol/dm^3, λ_{ex} = 310 nm). The inset shows a temporal profile of the emission at 420 nm. The relative amplitudes of the two nanosecond components were determined to be 0.89 (2.0 ns) and 0.11 (13 ns) at 420 nm. Corrections for detection sensitivity were made.

The picosecond time-resolved emission measurements clarified that the excited-state trimer is the dominant species in the subnanosecond region after photoexcitation and that larger oligomers are generated in the nanosecond region. To elucidate the earlier dynamics in the excited-state trimer, we measured femtosecond transient absorption with a time resolution of ~200 fs. Figure 3 shows the transient spectra at 0.1–10 ps (transient absorption spectra for $t > 10$ ps are shown in Figures S4 and S5.). A transient absorption band appeared around 600 nm immediately after photoexcitation and grew over 10 ps, showing a small blue shift with a small modulation of the peak wavelength in 1 ps (light blue arrow). Analysis of the temporal profile in the 450–650 nm region provided two time constants of 0.24 and 2.1 ps for this rise, and the pre-exponential factors were comparable at 600 nm (see Figure S3 for details). The 0.24 ps time constant is attributable to ISC, as it is close to the fluorescence lifetime of ~0.5 ps determined by fluorescence upconversion. The 2.1 ps time constant is much longer than that for ISC and typical time constants for internal conversion of metal complexes.[28,29] This Au trimer initially has a weakly bound loose structure in the S_0 state, where d_{Au-Au} is longer than 3 Å,[6,7] and it changes to a staggered structure having shorter d_{Au-Au} in the T_1 state in the picosecond time region. Therefore, it is highly likely that the 2.1 ps dynamics arises from the structural change occurring in the excited-state trimer after photoexcitation.

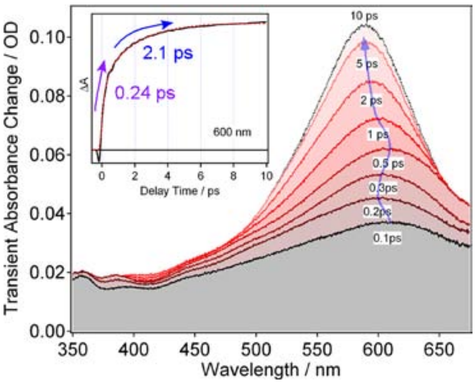


Figure 3. Femtosecond time-resolved absorption spectra of an aqueous solution of $K[Au(CN)_2]$ (0.28 mol/dm^3, λ_{ex} = 310 nm) at 0.1–10 ps. The light blue arrow denotes modulation of the transient absorption peak. The inset shows the time-resolved absorption signal at 600 nm.

To confirm the above assignment and elucidate the structural change giving rise to the observed spectral change, we performed density functional theory (DFT) calculations on the triplet excited-state trimer. The results showed that the optimized structure of the T_1 state is a linear staggered structure with d_{Au-Au} = 2.8 Å. Time-dependent DFT (TDDFT) calculations on this structure revealed a $T_n \leftarrow T_1$ transition at ~540 nm with a large oscillator strength (f = 0.7). This calculated $T_n \leftarrow T_1$ transition well-reproduced the observed transient absorption band. We also examined how the geometry of the trimer affected the $T_n \leftarrow T_1$ transition. The absorption spectra calculated as a function of d_{Au-Au} with the linear staggered form (Figure 4a) showed that the transition energy changed drastically, becoming higher with decreasing d_{Au-Au}, while the transition intensity remained almost constant. On the other hand, when we changed the Au–Au–Au bond angle from 180 to 130° with d_{Au-Au} fixed at 2.8 Å, the $T_n \leftarrow T_1$ transition intensity drastically decreased, although the transition energy exhibited only a moderate change (Figure 4b). In other words,

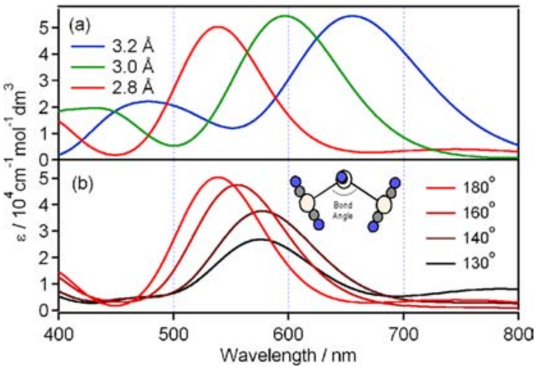


Figure 4. $T_n \leftarrow T_1$ absorption spectra calculated for the excited-state trimer as functions of (a) the Au−Au distance in the linear staggered structure and (b) the Au−Au−Au bond angle with d_{Au-Au} fixed at 2.8 Å. The other geometrical parameters were optimized. The full width at half-maximum of each absorption band was set at 3000 cm^{-1}.

the calculations indicated that the $T_n \leftarrow T_1$ transition exhibits a substantial intensity increase as well as a moderate blue shift when the excited-state trimer changes from the bent to the linear structure. This result excellently reproduces the temporal change of the transient absorption in the early picosecond time region. Therefore, we can safely conclude that the ∼2 ps growth of the transient absorption with a blue shift arises from the change from the bent to the linear structure in the excited T_1 trimer.

Although the shortening of the Au−Au bond occurs in the excited state with photoexcitation, the drastic blue shift of the transient absorption suggested by the TDDFT calculations was not observed in the transient absorption measurements. Nevertheless, as strong evidence for the shortening of d_{Au-Au} in the excited state, a low-frequency wave packet motion was clearly observed in the transient absorption in the femtosecond time region. As shown in Figure 3, the peak wavelength of the transient band was modulated in the femtosecond time region, and this was also recognized as an intensity modulation at particular wavelengths (Figure 5b and Figure S6). This oscillatory feature of the transient absorption is straightforwardly attributed to coherent nuclear motion induced by photoexcitation. Interestingly, the data show that the coherent motion survives in the ISC process.[24,25] The Fourier transform of the oscillatory component at 600 nm shows that the 66 and 87 cm^{-1} motions predominantly contribute to the oscillation (Figure 5c). Because they modulate the $T_n \leftarrow T_1$ transition energy, they are assigned to totally symmetric vibrations.[23,30]

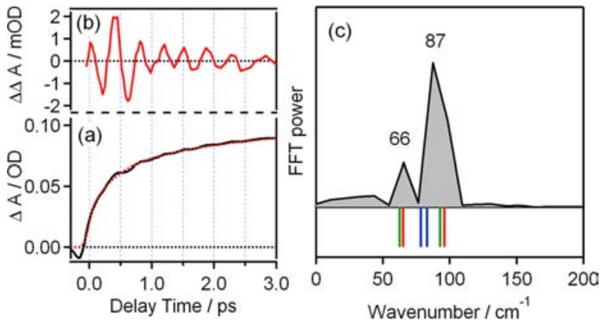
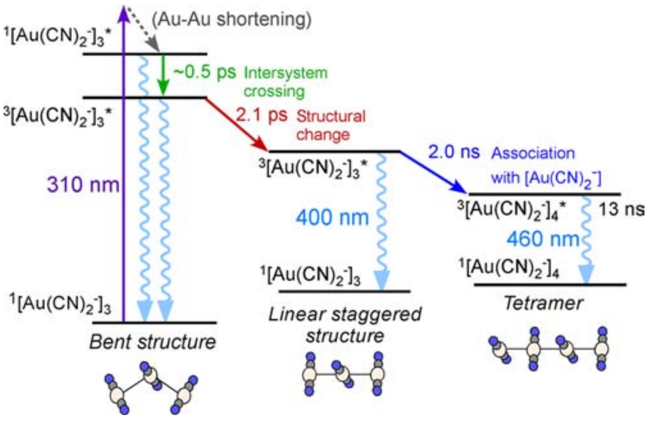


Figure 5. (a) Time-resolved absorption signal of the excited-state $[Au(CN)_2^-]_3$ trimer at 600 nm and (b) its oscillatory component. (c) Fourier transform power spectrum of the oscillatory component in (b). Red, green, and blue bars in (c) show the frequencies of the Au−Au breathing modes calculated by DFT at bond angles of 180, 160, and 140°, respectively.

The assignment of the observed coherent motion was made on the basis of DFT vibrational analysis of the triplet state of the $[Au(CN)_2^-]_3$ trimer. For the linear staggered trimer with D_{2h} symmetry, only two A_g modes were calculated in the frequency region of the interest (red bars in Figure 5c). Both modes include symmetric Au−Au stretching motions (Au−Au breathing motions; see Figure S7a,b). The calculated frequencies of these modes, 65 and 96 cm^{-1}, are close to the frequency of the observed nuclear motions in the femtosecond absorption. We also calculated vibrational frequencies of $[Au(CN)_2^-]_3$ at various Au−Au−Au bond angles. The frequencies of the two Au−Au breathing modes were calculated to be 63 and 93 cm^{-1} at 160° and 78 and 83 cm^{-1} at 140° (Figure S7c,d). Because of the weak dependence of the Au−Au breathing frequencies on the bond angle, it is difficult to derive clear information about the excited-state structure from the observed vibrational frequencies. Nevertheless, it is clear that the observed coherent motion is due to the Au−Au breathing motions induced upon photoexcitation. The weak angle dependence of the breathing-mode frequencies suggests that even though the structure of the S_0 state is widely distributed over the bending coordinate, well-defined coherent Au−Au breathing motions can be induced upon photoexcitation. This vibrational assignment is also consistent with the TDDFT calculations on the $T_n \leftarrow T_1$ transition (Figure 4a), which indicated that the change in the Au−Au bond length significantly affects the $T_n \leftarrow T_1$ transition energy, as we observed the coherent nuclear motion through the modulation of the peak position of the transient absorption. In fact, the Au−Au bond length differs significantly between the ground state ($d_{Au-Au} > 3$ Å[6,7]) and the excited states (calculated d_{Au-Au} = 2.8 Å). Thus, it is very natural that coherent Au−Au stretching (or shrinking) motion is induced by photoexcitation because the S_0 and S_1 potential curves are dislocated along the stretching coordinate. The shortening of the Au−Au bond is expected to occur on the time scale of the period of the 60−90 cm^{-1} Au−Au breathing motion (a few hundred femtoseconds). This implies that the bond shortening proceeds on a similar time scale as the ISC in this complex. However, no clear spectral change attributable to the Au−Au bond shortening process itself was observed in the present transient absorption measurements, probably because the bond shortening is completed in the excited singlet state, which exhibits only a small transient absorption intensity.

On the basis of the results of the present study, the ultrafast dynamics of photoexcited $[Au(CN)_2^-]_3$ trimers is sketched in Scheme 1. In the ground state, the Au−Au bonds are weak (∼0.1 eV),[6] and the trimers do not have a rigid geometry but are present in loose bent geometries. The structure is distributed along coordinates corresponding to very low frequency vibrational modes such as bending. Upon photoexcitation, the Au−Au bonds become substantially stronger and the bond lengths are quickly shortened, after which ISC occurs in a few hundred femtoseconds. The drastic Au−Au bond change induces coherent nuclear motion in the excited state, which is observed as the modulation of the peak of the transient absorption in the early picosecond region. The shortening of the Au−Au bonds also induces a significant increase in the steric and/or electrostatic repulsion among the CN groups, causing the initial loose structure to change into the linear

Scheme 1. Relaxation Pathways for Excited-State $[Au(CN)_2^-]_3$ in Aqueous Solution (~0.3 mol/dm^3)



structure in the triplet state, which takes several picoseconds. The blue shift and the rise of the transient absorption observed up to 10 ps is attributed to this structural change. Finally, association of the complex occurs in a few nanoseconds, and larger oligomers are formed.

Ultrafast spectroscopic measurements and complementary theoretical calculations have unveiled the ultrafast dynamics of structural changes in $[Au(CN)_2^-]_3$ oligomers. A distinct oscillation of the transient absorption was observed in the femtosecond time region, providing clear evidence of the drastic shortening of the Au−Au distances in the excited state of the oligomer. In this regard, this work presents a "snapshot" of the formation of tight Au−Au bonds in oligomers recorded by time-resolved spectroscopy. Because $[Au(CN)_2^-]_n$ provides a fundamental system in which metal−metal bond formation, large structural changes, and association of oligomers with monomers can be examined, we can learn details about the elementary processes of metal complexes from time-resolved studies of this system.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Concentration dependence of the absorption spectra of $[Au(CN)_2^-]$ aqueous solutions, selective excitation of the trimer with 310 nm light, fluorescence decay profile measured with upconversion, analysis of the temporal profile of the femtosecond time-resolved absorption signal, transient absorption spectral shift at 10−1000 ps, transient absorption spectra in the nanosecond region, wavelength dependence of the modulation in the transient absorption signal, normal coordinates of Au−Au breathing modes, details of quantum-chemical calculations and the calculation of the diffusion rate constant using the Debye−Smoluchowski equation, and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by KAKENHI, Grant-in-Aid for Young Scientists (B) (23750060), and Grants-in-Aid for Scientific Research (C) (22550057) and (A) (22245005).

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