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Lanthanide Organometallic Sandwich Nanowires: Formation Mechanism

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A molecular beam of europium−cyclooctatetraene sandwich nanowires $Eu_n(COT)_m$ was produced by a laser vaporization synthesis method. The formation mechanism of the nanowires was quantitatively revealed by photoelectron and photoionization spectroscopies of the Eu−COT species, together with supporting theoretical calculations. From these results, it is confirmed that growth processes extending the length of Eu−COT nanowires involve a series of elementary reactions in which efficient charge transfer occurs at the terminal reaction sites. In every elementary step, the reaction proceeds between one reactant having low ionization energy and the other reactant having high electron affinity, probably via a “harpoon” mechanism.

Metal−ligand sandwich systems continue to attract the attention of scientists, a half century following the discovery of the first sandwich complex ferrocene, Fe $(\eta^5\text{-}C_5H_5)_2$.[1] Recently, there has been renewed interest in multilayer sandwich compounds.[2] The regulation of electronic and magnetic interactions between metal atoms in organometallic complexes has been investigated, for example, through studies of charge transfer in linear chains of alternating metallocenium donors and polycyano hydrocarbon acceptors.[3] Although many synthetic experiments have been conducted on organometallic complexes in the condensed phase, various environmental factors such as oxidation or reduction of the products can make these approaches problematic. Since the advent of laser vaporization synthesis methods, molecular beam techniques have offered ideal environments for the production and characterization of novel species and for probing chemical reactions and solvation phenomena involving metal atoms/ions.[4]

Recently, we reported the synthesis of a multilayer sandwich complexes composed of vanadium (V) and benzene (Bz) in the gas phase using a combination of laser vaporization techniques and molecular beam methods.[5] In practice, we find that the length of these one-dimensional (1-D) $V_n(Bz)_m$ complexes is limited to ∼7 layers, because the V atoms must be prepared in electronically excited states to have sufficient reaction probabilities. Similar 1-D stacking was achieved in lanthanide (Ln) complexes using 1,3,5,7-cyclooctatetraene (C_8H_8; COT) molecules as ligands.[2,6] In contrast to $V_n(Bz)_m$, growth of $Ln_n(COT)_m$ complexes can occur with abundant ground-state Ln atoms as reactants, thus enabling the production of large complexes ($n > 10$). From the analysis of their electronic structures, these Ln−COT sandwiches were highly ionic species, in which the Ln atoms are in most cases trivalent (Ln^{3+}) and in some cases (e.g., europium (Eu)), divalent (Ln^{2+}). In this study, we report efficient gas-phase formation of Eu−COT sandwich nanowires, with selective 1-D stacking up to 18 layers. We also present an analysis of the formation mechanism, based on quantitative evaluation of photoelectron (PE)/photoionization spectroscopic experiments and supporting theoretical calculations.

Details of the experimental setup have been described elsewhere.[2] Briefly, $Eu_n(COT)_m$ complexes were synthesized via the gas-phase reaction between laser-vaporized Eu atoms and COT molecules. The beam was mass-analyzed using a time-of-flight (TOF) mass spectrometer with photoionization by an ArF excimer laser (6.42 eV) or a wavelength tunable laser (6.3−3.5 eV). The PE spectra of the Eu−COT complex anions were measured using a magnetic bottle TOF photoelectron spectrometer. To compare the electronic structures, the PE spectra of barium (Ba)−COT complex anions were also measured with the identical setup except for the use of a Ba target. The mass-selected complex anions were photodetached with the third or fifth harmonic (355 or 213 nm) of a Nd^{3+}:YAG laser.

Figure 1 shows typical examples of photoionization mass spectra of $Eu_n(COT)_m$ complexes [henceforth abbreviated as (n, m)]. The predominant mass peaks for complexes having a given n show almost the same compositions, namely (n, $n + 1$), (n, n), and (n, $n - 1$). As reported previously in studies of transition metal−Bz complexes, such as V−Bz,[5] this regular pattern in the mass spectra implies that the complexes possess multilayer sandwich structures in which Ln ions stack alternately with COT ligands: three series of (n, $n + 1$), (n, n), and (n, $n - 1$) can be ascribed to full sandwiches, one-end-open sandwiches, and both-ends-open sandwiches.

The striking difference between Eu−COT and V−Bz complexes is the maximum length that can be achieved using the laser-vaporization synthesis method. As shown in Figure 1b,

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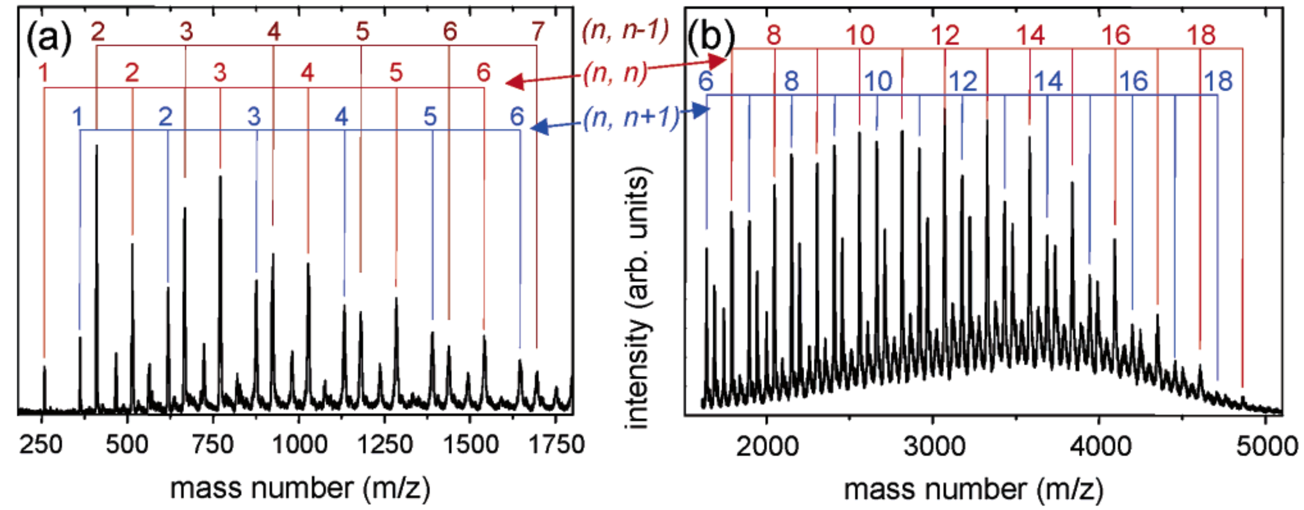

Figure 1. Time-of-flight mass spectra of Eu−COT neutrals obtained by photoionization of ArF laser (6.42 eV): (a) low mass range and (b) high mass range. In (b), peak assignments for (n, n − 1) are removed for clarity.

Eu−COT sandwiches were formed with up to 18 layers (about 8 nm overall length). In contrast, the maximum size of V−Bz sandwiches was limited to about 7 layers even with the recently implanted production enhancement involving the use of dual V rods.[5b] This difference in size distributions for the two systems can be traced to the difference in the bonding characteristics; the metal−ligand bonding in Eu−COT is highly ionic, whereas that in V−Bz complexes is covalent. Growth processes that extend the length of Eu−COT chains clearly involve a series of elementary processes in which an alternating piling up of Eu atoms and COT ligands occurs. Because the Eu−COT sandwiches consist of positively charged Eu ion and negatively charged COT, the successive reaction likely proceeds with an electron transfer from Eu to an Eu−COT intermediate or from an Eu−COT intermediate to COT, satisfying the charge distribution. As seen in the prototypical example of provided by the Li + F_2 “harpoon” reaction,[7] the reaction path is “downhill all the way”—no barrier at all, when electron transfer takes place and an ion pair (e.g., $Li^+F_2^-$) is formed at the first stage of the reaction.

When a full sandwich of $Eu_n(COT)_{n+1}$ undergoes further reaction to extend its length, four processes I−IV are conceivable: A Eu atom is attached to one of the terminal COTs of (n, n + 1) (process I). When a one-end-open sandwich of (n, n) extends the length, a COT ligand may be attached to the terminal Eu atom of (n, n) (process II). If the addition of the second Eu atom to (n, n) occurs before the COT termination (process III), a both-ends-open sandwich [$Eu_n(COT)_{n-1}$] is abundantly formed, as actually seen in Figure 1. By terminating one of the two Eu ends in $Eu_n(COT)_{n-1}$ with COT, a one-end-open sandwich is produced (process IV).

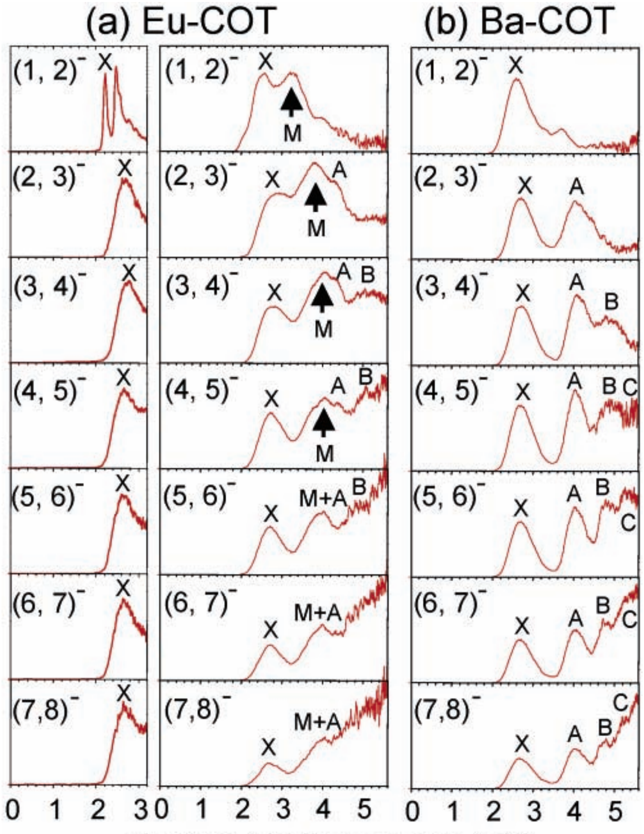

Figure 2. Photoelectron spectra for full sandwich (n, n + 1) anions of (a) Eu−COT^- at 355 and 213 nm (3.49 eV/5.82 eV) and (b) Ba−COT^- at 213 nm (n = 1−7). The electronic bands from COT (X, A, B, ...) and from Eu 4f orbitals (M) are assigned by comparison between Eu−COT^- and Ba−COT^-.

For an elementary reaction to occur via the harpoon mechanism, one reactant must possesses a low ionization energy (E_i) and the other reactant a high electron affinity (EA).[7] To examine the reaction mechanism given by processes I and II, quantitative knowledge of the EA of (n, n + 1) and E_i of (n, n) is necessary. Toward these ends, we have conducted PE spectra experiments of the full sandwich anions, $Eu_n(COT)_{n+1}^-$ (n = 1−7) (Figure 2a). The 213 nm PE spectrum recorded for the full sandwich anions yields a vertical detachment energy (VDE) of ∼2.5 eV and an adiabatic detachment energy of ∼2.1 eV. The latter is taken to be the EA of the full sandwich of (n, n + 1). To assign the photoelectron spectra more conclusively, we have also measured PE spectra for the full sandwich anions of $Ba_n(COT)_{n+1}^-$ (n = 1−7) at 213 nm (Figure 2b). Because Ba atoms preferably assume +2 oxidation state in these complexes (as do Eu atoms), the PE spectra of $Ba_n(COT)_{n+1}^-$ reflect simpler electronic structures, because electrons are photodetached only from COT^{x-} ligands without complications due to photodetachment of 4f electrons. In fact, the mass distributions of anionic and neutral $Ba_n(COT)_m$ were almost identical to those of $Eu_n(COT)_m$ shown in Figure 1. As expected in view of the identical ionic bonding patterns exhibited by $Eu_n(COT)_{n+1}^-$ and $Ba_n(COT)_{n+1}^-$,

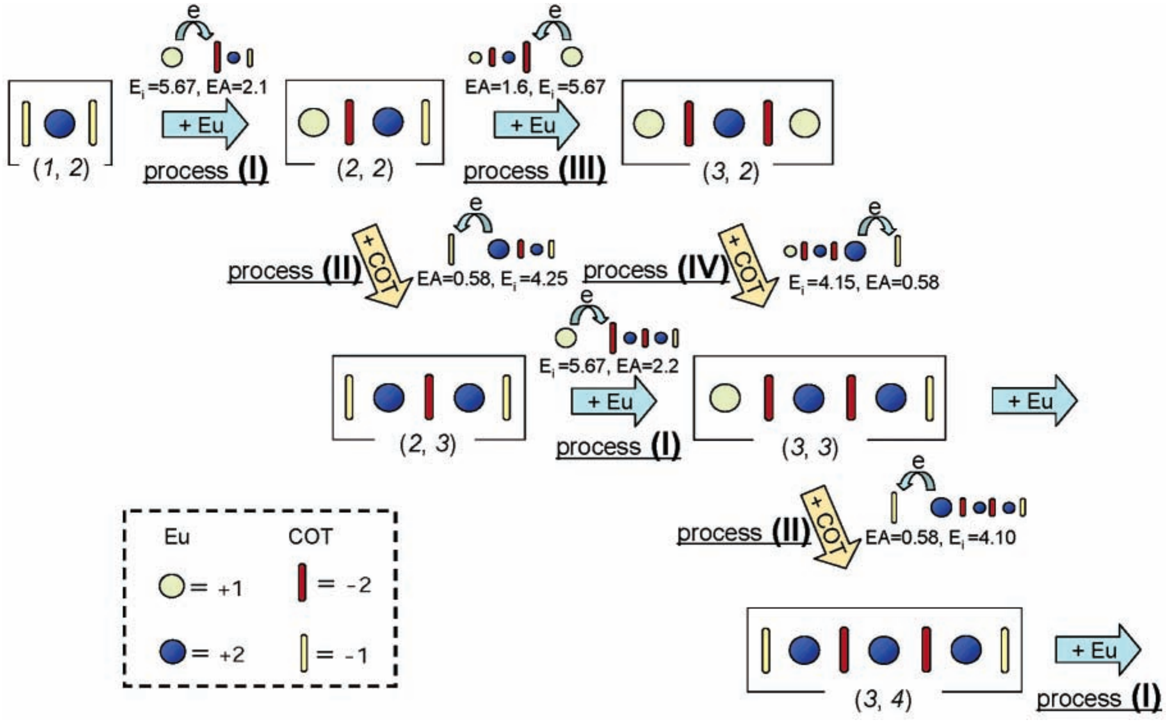

Figure 3. Energetics of Eu−COT growth was experimentally evaluated by photoelectron and photoionization spectroscopies. In every elementary step, the reaction proceeds between one reactant having low ionization energy and another reactant having high electron affinity, preferably via a "harpoon" mechanism. The endoergicity, ΔE_0, is calculated to be 3.5−4.0 eV and the largest separation R_x at which charge transfer can take place on energetic grounds is evaluated to be 4 Å. Values of ionization energy (E_i) and electron affinity (EA) are given in electronvolts. The reaction scheme shown here for $n = 1-3$ is general, applying to any n, thus enabling rapid, sequential growth leading to production of very long sandwich nanowires (up to $n = 18$).

both systems give almost the same EA and display similar overall features (Figure 2), whereas there is apparently an additional photodetachment contribution of 4f orbitals around 3−3.5 eV in the spectra of $Eu_n(COT)_{n+1}^-$: a channel from Eu^{2+} to Eu^{3+} (labeled by "M" in Figure 2a). As shown in Figure 2b, the spectra at larger n display additional discrete transitions at higher binding energies (A, B, C, ...). Our DFT calculations[8] show with reasonably certainty that, in view of the strong ionic character of the Eu−COT bonding, the binding energy of electrons on each COT^{2-} ligand critically depends on the position in the complexes: the one of the outermost COT^{2-} is the lowest, corresponding to the peak X, yielding EA, and it increases in going to the central COT^{2-} and converges to around 6 eV at larger n (the right edge of the spectra). An electron transfer to the outermost COT^{2-}, a crucial step in process I, can thus take place readily.

The E_i of the one-end-open $Eu_n(COT)_n$ sandwiches were measured by photoionization spectroscopy. The ionization thresholds for $Eu_n(COT)_n$ ($n = 1-4$) occur at 6.12, 4.25, 4.10, and 4.01 eV, respectively. With increasing size, the ionization energy drops drastically. According to the DFT calculations,[8] the observed drop in E_i with increasing size results from the ionic character of Eu−COT: they can be 1-D stacks of a dipole array consisting of alternating $Eu^{2+}COT^{2-}$ units. The HOMO of the terminal Eu of $Eu_n(COT)_n$ is successively destabilized with addition of dipole units of $Eu^{2+}COT^{2-}$, and the terminal Eu stays not as Eu^{2+} but as Eu^{1+}, which is then ready to proceed in the next reaction of the formation of the full sandwich because of the low E_i of $Eu_n(COT)_n$.

Based on this quantitative evaluation of the EAs and the E_i of Eu−COT complexes, a simple estimate of the range of the harpoon event can be obtained by considering the energetics of the charge transfer (see Figure 3). In process I, an electron transfers from a Eu atom to a full sandwich, and the corresponding endoergicity, ΔE_0, is calculated to be 3.6 eV from the E_i of Eu atom (5.67 eV)[9] and the EA of $Eu_n(COT)_{n+1}$ (about 2.1 eV). The largest separation R_x at which charge transfer can take place on energetic grounds is evaluated to be 4 Å. Similarly, R_x in process II is evaluated to be 3.9−4.2 Å except for the reaction of $Eu_1(COT)_1$ + COT, using the E_i of $Eu_n(COT)_n$ ($n = 2-4$: 4.3−4.0 eV) and the EA of COT (0.58 eV).[9] These R_x values in processes I and II are actually large enough to have a reaction probability so as to allow successive growth in length, thus favoring production of sandwiches having larger n.

Similarly, for processes III and IV, experimental and theoretical considerations support an efficient charge-transfer process; the EA of one-end-open sandwich of $Eu_n(COT)_n$ are high ∼2.1 eV for $n = 1-5$ whereas the E_i of both-ends-open sandwich of $Eu_n(COT)_{n-1}$ are low ∼4.2 eV for $n = 2-4$. In every elementary reaction, a charge transfer efficiently occurs at the terminal reaction sites at large R_x, and the formations are fast exoergic reactions that have no reaction barrier. The mechanism analysis presented here reveals why it is possible to make Eu−COT sandwich nanowires as long as 8 nm length. As well as being prototypical anisotropic quantum wells possessing 1-D structures, these sandwiches may display interesting and potentially useful optical and magnetic properties and thus serve as 1-D building blocks in nanostructured materials. Work toward exploring these possibilities is currently underway.

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