

## The Electronic Structures of Terbium-Phthalocyanine Sandwich Clusters

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Terbium (Tb)-phthalocyanine (pc) sandwich clusters,  $Tb_n(pc)_{n+1}$  ( $n = 1-4$ ), and their Na adducts,  $TbNa_k(pc)_2$  ( $k = 1-4$ ) were produced by dual laser vaporization of a Tb rod and the molded rod of metal-free or disodium phthalocyanine ( $H_2pc/Na_2pc$ ) in gas phase. The minimum number of Na atoms attached to the cationic/neutral/anionic  $Tb_1(pc)_2$  clusters is 2, 1, and 0, respectively. Together with the ionization energies of the Na adducts of  $Tb(Na)_k(pc)_2$  ( $k = 1$  and 2), it is revealed that the Tb-pc clusters are formed through fairly ionic bondings, where each component exists as  $Tb^{3+}$ ,  $Na^+$ , and  $pc^{2-}$ , respectively.

Phthalocyanine (pc) is one of the most popular  $\pi$ -conjugated macrocyclic molecules. It is well known that most of metal elements form pc complexes, and some of them have attracted a great deal of attention because of their unique properties such as semiconductivity, photoconductivity, and chemical activity.<sup>1,2</sup> Several bis(phthalocyaninato)lanthanide(III) complexes have been synthesized and their geometric structures have been determined by X-ray crystallographic studies.<sup>6,7</sup> They are actually expected to serve as active materials for molecular devices such as electrochromic displays and chemical sensors.<sup>1-5</sup> A similar stacking structure has been found for the complex of In, Zr, U, etc., and triple decker phthalocyanine complex has also been synthesized.<sup>8-12</sup> In particular, lanthanide-pc multiple-decker sandwich complexes are very attractive for molecular information storage applications because of their large number of available oxidation states,<sup>11</sup> and electronic structure of  $[Lu(pc)_2]$  has been investigated.<sup>3,12,13</sup>

Gas phase synthesis enables us to generate novel metal-ligand complexes and to utilize several powerful spectroscopic means to characterize them.<sup>14</sup> One of the advantages of the gas phase experiment is elimination of environmental effects such as solvents or counter ions. This enables us to investigate the intrinsic properties and interaction between metal atom and ligand. As demonstrated previously in the formation of lanthanide organometallic clusters, it has been revealed that  $Ln_n(C_8H_8)_m$  clusters are preferably formed as multiple-decker sandwich clusters.<sup>15</sup>

In this letter, we will report the multiple-decker sandwich structure of terbium (Tb)-pc cluster produced by the laser vaporization in gas phase. Mass spectrometry for the Na atom adducts of the Tb-pc clusters reveals electronic structures, as well as the measurements of their ionization energies.

The  $Tb_n(pc)_m$  clusters were produced by the combination of laser-vaporization, laser-desorption, and molecular beam method. The experimental setup used in this work has been described elsewhere.<sup>14-16</sup> Briefly, metal-free or disodium phthalocyanine ( $H_2pc/Na_2pc$ ) coated on a stainless steel rod was ablated gently by a  $Nd^{3+}:YAG$  laser, and the pc vapor was mixed with Tb atom vapor generated by the other  $Nd^{3+}:YAG$  laser. After being cooled

inside a channel by pulsed He carrier gas (6 atm stagnation pressure), the mixed vapors were expanded into the vacuum. Generated clusters were sent to the second chamber through a skimmer. The neutral clusters were ionized by the ArF laser (193 nm, 6.42 eV) or the second harmonic output of OPO laser (290–220 nm) or its mixing output with the fundamental of a  $Nd^{3+}:YAG$  laser (223–193 nm), and the photoions were accelerated in a static extraction field (3 kV). On the other hand, cluster ions in the beam were directly accelerated with a fast pulsed electric field. The ions were mass analyzed with a time-of-flight mass spectrometer equipped with a reflectron. The signal was accumulated in a transient oscilloscope.

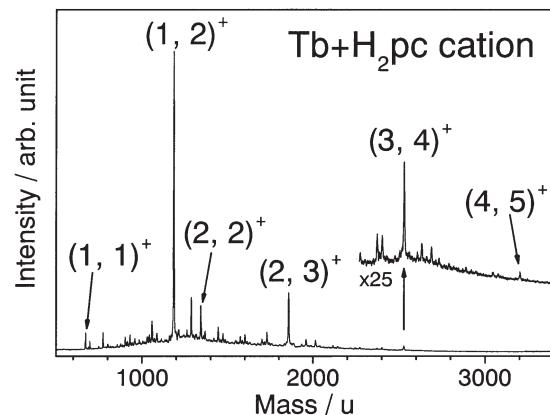
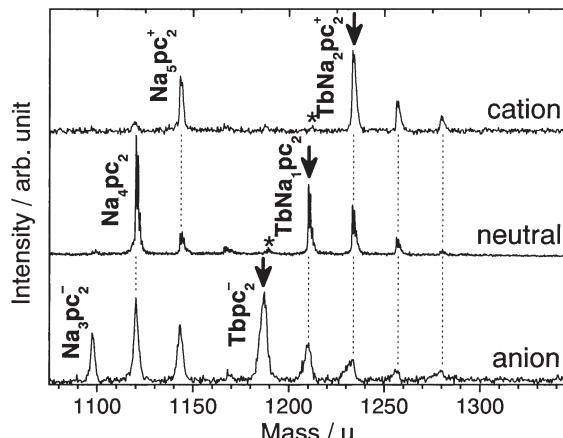


Figure 1. Mass spectrum of cationic terbium-phthalocyanine clusters. Peaks are labeled by the notation of  $(n, m)$ , denoting the numbers of Tb atoms ( $n$ ) and phthalocyanine molecules ( $m$ ).

Figure 1 shows a mass spectrum of positively charged  $Tb_n(pc)_m$  clusters produced by the dual laser ablation of Tb metal and  $H_2pc$ . The abbreviation of  $(n, m)$  means that cluster consists of  $n$  Tb atoms and  $m$  pc ligands. The most abundant cluster is  $(1, 2)$ , and the predominant species can be assigned to the composition of  $(n, n+1)$  ( $n = 1-4$ ). Dehydrogenations of  $H_2pc$  ligands were accompanied; for example, major product of  $(1, 2)$  was two H-atoms eliminated species. No formations of  $(n, n+2)$  clusters imply that the metal atoms are sandwiched by the pc ligands. Furthermore, when fluorine gas diluted by He (5% of  $F_2$ ) was injected into the channel, no adduct was formed for  $(1, 2)$ , while fluorinated adducts of  $(1, 1)$  and  $(2, 2)$  were produced. The result of no reactivity of  $(n, n+1)$  evidently shows that laser-synthesized  $(n, n+1)$  clusters in gas phase take a sandwich structure similar to the complexes synthesized in condensed phase.<sup>5-9</sup> Intensities of larger clusters decrease rapidly. This is probably because the reaction time within the cluster source is relatively too short to form the clusters.

Replacing the source of pc ligand by disodium phthalocyanine ( $Na_2pc$ ), the charge distribution in the cluster can be determined without ambiguity of mass overlapping between

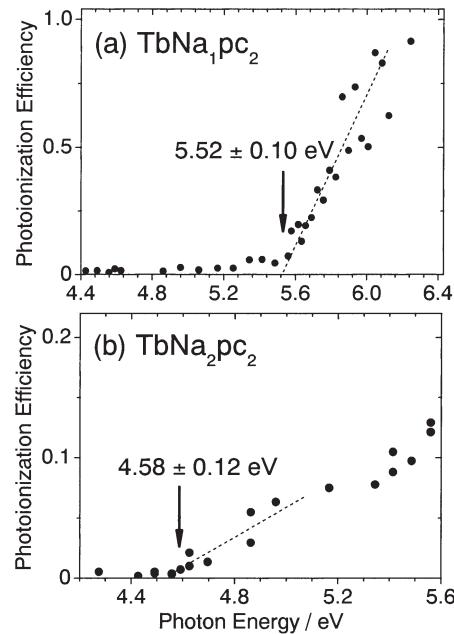


**Figure 2.** Mass spectra for  $\text{Tb}_n\text{Na}_k(\text{pc})_m^{+/-0/-}$ . Arrows indicate the magic numbered clusters which strictly satisfy the oxidation states of  $\text{Tb}^{3+}$ ,  $\text{pc}^{5-}$ , and  $\text{Na}^+$ . Peaks labeled with asterisk are assigned to  $\text{Na}_k(\text{pc})_2^{+/-0/-}$  clusters.

hydrogenated species. Figure 2 shows a part of mass spectra of cationic, neutral, and anionic clusters,  $\text{Tb}_n\text{Na}_k(\text{pc})_m^{+/-0/-}$  for  $m = 2$ . The mass patterns of the  $\text{Tb}_n\text{Na}_k(\text{pc})_2$  clusters clearly shift depending on the total charge on the clusters. Namely, the minimum numbers of Na atoms for  $\text{Tb}_1\text{Na}_k(\text{pc})_2^{+/-0/-}$  are  $k = 2, 1$ , and 0, whereas those for  $\text{Na}_k(\text{pc})_2^{+/-0/-}$  are  $k = 5, 4$ , and 3. This magic numbered behavior can be ascribed to the nature of charge-transfer complexes as follows: Tb atoms and Na atoms are supposed to take +3 and +1 oxidation states, whereas pc ligand takes -2 oxidation state. The latter is because the total number of the  $\pi$ -electrons in the macrocycle of  $\text{pc}^{2-}$  is 18, where the Hückel rule of  $4n + 2$  is satisfied as  $n = 4$ . Then, magic numbers are explained well by the charge allotment as follows:  $\{\text{Tb}^{3+}(\text{Na}^+)_2(\text{pc}^{2-})_2\}^+$ ,  $\{\text{Tb}^{3+}(\text{Na}^+)_1(\text{pc}^{2-})_2\}^0$ ,  $\{\text{Tb}^{3+}(\text{pc}^{2-})_2\}^-$ . Since this charge distribution is also applicable to explain the mass distribution of  $\text{Na}_k(\text{pc})_m^{+/-0/-}$  clusters, an ionic bonding character well describes these phenomena rather than the covalent one. It should be noted that Na atoms are overdosed in this experiment because pc ligands are supplied by  $\text{Na}_2\text{pc}$ . The elimination of Na atoms can be controlled by varying the vaporization laser power: Higher laser fluence enhances the Na elimination. This can seemingly be explained by that excess energy in the clustering process is released by Na detachments.

Figure 3 shows photoionization efficiency (PIE) curves for (a)  $\text{TbNa}_1(\text{pc})_2$  and (b)  $\text{TbNa}_2(\text{pc})_2$  clusters. The ionization energies ( $E_i$ ) for  $\text{Tb}_1\text{Na}_1(\text{pc})_2$ , and  $\text{Tb}_1\text{Na}_2(\text{pc})_2$  clusters were determined as  $5.52 \pm 0.10$  eV and  $4.58 \pm 0.12$  eV from the slope in the first onset. This large change in  $E_i$  can be explained by the electron filling in molecular orbitals of pc ligands.

The molecular orbitals of ligand pc moiety are filled by electrons transferred from Tb and Na atoms. The HOMOs and LUMOs of (1, 2) are characterized as  $2a_{1u}/2b_1$  and  $6e_3/6e_1$ , which are formed from the degeneration of  $2a_{1u}$  and  $6e_g$  of two pc ligands, respectively.<sup>10</sup> Without Na atoms, the HOMO of (1, 2) has one electron vacancy because Tb atom donates 3 electrons to the HOMOs. This vacancy can be filled by one electron from one Na atom. With two Na atoms, however, electrons donated by Na atoms are accommodated also to the LUMO ( $6e_3$ ) of (1, 2). Then the  $E_i$  for two-Na adduct is much lower than that of one-Na adduct. Indeed the PIE curves of  $\text{Tb}_1\text{Na}_k(\text{pc})_2$  for  $k = 2-4$  exhibit the second onset around 5.6 eV which can be assigned to



**Figure 3.** Photoionization efficiency curves for (a)  $\text{TbNa}_1(\text{pc})_2$ , and (b)  $\text{TbNa}_2(\text{pc})_2$ . Down arrows indicate the position of ionization energies.

ionization channel from the filled  $2a_2$ .

In summary, the Tb–pc mixed clusters can be generated by laser vaporization of Tb and pc, and they favorably form a sandwich structure. The mass distribution and ionization energies of Na adducts of  $\text{Tb}_1(\text{pc})_2$  can reveal that the electric properties are characterized by charge-transfer complexes through fairly ionic bondings.

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