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Tunable photo-induced electronic property of octahedral metal clusters

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ABSTRACT

The tunable photo-induced electronic property of the $Cs_2[\{Mo_6Br^i_8\}Br^a_6]$ and $Br_2[\{Ta_6Br^i_{12}\}(H_2O)^a_6]$ octahedral metal cluster-based compounds was characterized by the zeta potential measurement upon irradiation by ultraviolet–visible (UV–Vis) light. The enhancement of the electronic charge on the surface of the $[\{Mo_6Br^i_8\}Br^a_6]^{2-}$ cluster-based anion caused by the irradiation increased the negative zeta potential. Both compounds showed the dependence of the zeta potential as a function of the light excitation. This will be a promising property for sensor applications based on the reversibility of the photo-electrochemical properties of the functional cluster.

1. Introduction

Multifunctional materials based on the integration of an organic–inorganic atomic integrated system that demonstrate the reversibility of redox transformation, photochemistry, or electrochemistry are attracting attention for energy-saving applications such as photovoltaics [1] and light-emitting diodes (LEDs) [2]. As is known, the metal atom cluster (MC) family, which is built either on an edge-bridged $\{M_6(\mu_2\text{-}X^i)^i_{12}\}$ (M = Ta, Nb, W) or face-capped $\{M_6(\mu_3\text{-}X^i)^i_8\}$ (M = Mo, Re) metallic cluster core (X^i = I, Br, Cl) coordinated with apical ligands (L^a = I, Br, Cl, H_2O, OH) with a nanometer size (under 2 nm) exhibiting photochemical and photophysical [3], luminescent [4], and redox properties [5], have been extensively studied. Generally, the valence electron counts (VEC) are equal to 24 electrons or 16 electrons on the electron shell per the $[\{M_6(\mu_3\text{-}X)^i_8\}L^a_6]^{2-}$ or $[\{M_6(\mu_2\text{-}X)^i_{12}\}L^a_6]^{4-}$ cluster unit, respectively, and it will become a strong and powerful oxidant in the oxidized state[6–7]. The luminescence of MC has been remarkably studied for the $\{M_6(\mu_3\text{-}X)^i_8\}^{4+}$ metallic core cluster that results in a strong light emission in the red/near-infrared light range which could be quenched by oxygen to generate singlet oxygen [8–10]. In addition, the redox photochemistry of the $\{M_6(\mu_2\text{-}X)^i_{12}\}^{2+}$ metallic core can be used to form $\{M_6(\mu_2\text{-}X)^i_{12}\}^{3+/4+}$ species in an electric field [11]. The detailed studies are progressing to determine a new tunable process between the electronic, optical, and chemical properties of the cluster by using further techniques. The reversion between the optical and electrochemistry of the $[\{Mo_6I^i_8\}Cl^a_6]^{2-}$ cluster studied by chemical and electrochemical methods has been reported [12–14]. The deposition of the negative $[\{M_6(\mu_3\text{-}Br)^i_8\}Br^a_6]^{2-}$ and positive $[\{M_6(\mu_2\text{-}X)^i_{12}\}(H_2O)^a_6]^{2+}$ charged cluster on ITO-coated glass was successfully prepared by electrophoretic deposition and the film-forming mechanism was reasonably proposed [15–16]. It is known that the control of the surface charge potential is a fundamental processing parameter for the EPD process. However, how to control the surface charge of the cluster has not yet been investigated. In this study, we first investigated the effect of the light absorbing characteristic on the charging property by excited electron transfer in the $[\{Mo_6(\mu_3\text{-}Br)^i_8\}Br^a_6]^{2-}$ cluster and $[\{Ta_6(\mu_2\text{-}Br)^i_{12}\}(H_2O)^a_6]^{2+}$ cluster units. An electro-osmosis analysis was used to measure the zeta potential on the charged surface of the cluster unit in an organic solvent during light irradiation. The interesting behavior of the zeta potential versus the photon energy from light irradiation has been determined.

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2. Experimental

The study was performed using two kinds of MCs: i) a suspension of the $Cs_2[\{Mo_6Br^i_8\}Br^a_6]$ compound (CMB) prepared in methyl ethyl ketone (MEK, 99%) at a concentration of 0.75 g/l; and ii) a suspension of the $Br_2[\{Ta_6Br^i_{12}\}(H_2O)^a_6]$ compound (TBH) dispersed in acetone/distilled water (100/4) at a concentration of 1 g/l. The MCs were synthesized as reported in refs. 11 and 17 without purification [11,17]. Acetone or MEK are the best solvents for the EPD process of the Mo_6 cluster-based compounds as already reported [15], while acetone/H_2O allows the $[Ta_6Br^i_{12}(H_2O)^a_6]^{2+}$ species to remain active in the green-colored TBH suspension and slows down the oxidation of TBH [16]. The cluster structure scheme and optical absorbance of the MCs in solution are presented in Fig. 1a and b. The green-colored TBH suspension displayed a strong absorbing peak at 350 nm and a weaker absorbing peak at 425 nm, while the yellow-colored CMB suspension showed a broad absorbing band from 320 nm to 500 nm. These results agreed with previous studies [15–16].

The zeta potential (ZP) and conductivity of the MC suspensions were measured by using a zeta-potential and particle size analyzer equipped with a green laser (ELSZ-2000 series). A green light source was created by a high power semiconductor laser that was selected with the purpose to reduce the light-absorbing and emitting effects caused by the MC. The cell temperature was not changed even after light irradiation, because the heat-capacity of the solution is very large, and the heat formed by the light absorption is small enough to increase the temperature of the system. The scheme of the quartz cell and the measurement system is presented (Fig. 1c). The absorbance and photoluminescence characterizations were studied.

3. Results and discussion

In Fig. 1d and 1e, the ZP values were recorded at 24.9 mV and −34.7 mV for TBH and CMB, respectively. These results agreed with the assumption that they are positively charged $[\{Ta_6(\mu_2\text{-}Br)^i_{12}\}(H_2O)^a_6]^{2+}$ and negatively charged $[\{Mo_6(\mu_3\text{-}Br)^i_8\}Br^a_6]^{2-}$ cluster units [7,15–16].

CMB in MEK excited at the wavelength of 370, 410, and 440 nm by using the Xenon lamp results in a fluorescence light emission with a broad peak at 685 nm (Fig. 2a). Based on this result, all suspensions were irradiated for 10 min, then stopped before starting the ZP measurement. In Fig. 2b, the ZP of CMB without irradiation was −35.9 ± 0.2 mV that was based on 5 measurements. The electric conductivity was about 0.095 mS/cm which was almost unchanged for the different wavelengths. Considering this result, the property of the CMB suspension (pH, concentration) is relatively stabilized under the applied voltage. With the irradiation at 540 nm, the value was unchanged due to the weak absorption of CMB at this wavelength. Upon irradiation at 440, 410, and 370 nm, the tendency of the negative value increase corresponds to the higher optical absorbance of the CMB. The amount of the excited electrons on the charged particle surface predictably

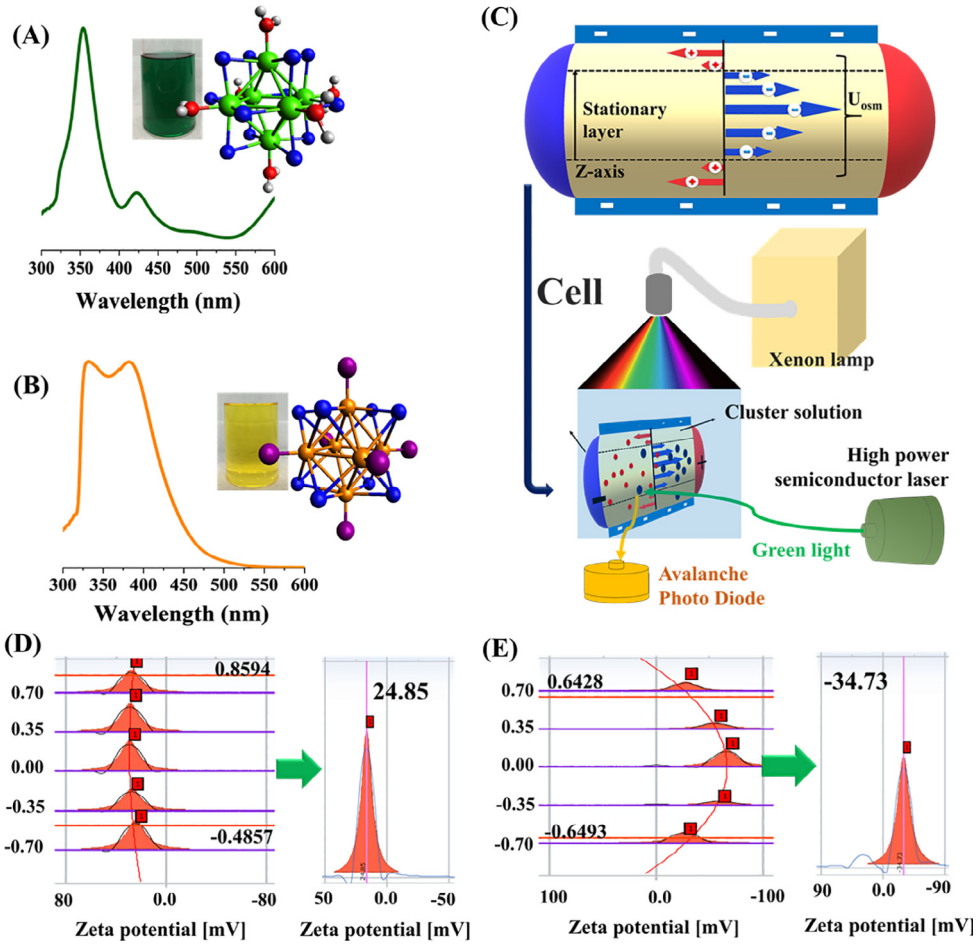

Fig. 1. Optical absorption, MC scheme of A) TBH in acetone/water and B) CMB in MEK. C) Model of the quartz cell and ZP measurement equipped with light irradiation. The ZP value of D) TBH, and E) CMB.

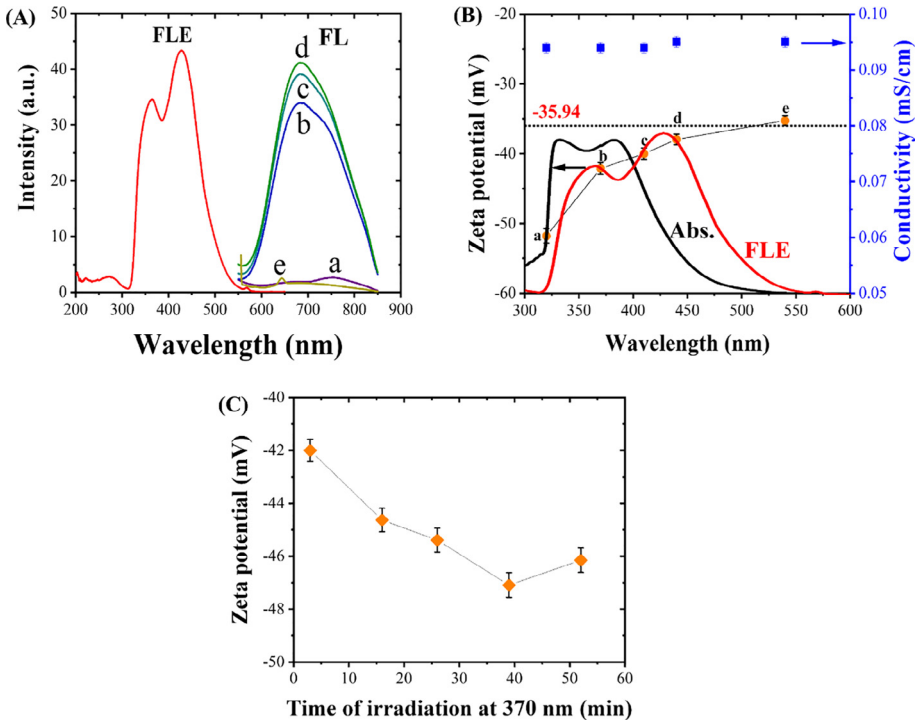

Fig. 2. A) Fluorescence (FL) and fluorescence excitation (FLE) spectra of emission light at 685 nm, B) The dependence of the ZP and electric conductivity of CMB in MEK excited at different wavelengths, and C) ZP versus the irradiation time at 370 nm. The excitation wavelengths of 320, 370, 410, 440, and 540 nm were denoted as the a, b, c, d, and e symbols, respectively.

increases due to the enhancement of the exciting electrons caused by the light absorption in the required range. The negative ZP of CMB when excited at 320 nm reached a maximum of −51.8 ± 0.3 mV. This point, which does not follow the regular tendency due to the absorption without luminescent emission irradiated at 320 nm, was confirmed in Fig. 2a. The total photon energy which excites electrons will not be lost by the light emission. ZP versus time was continually performed for 55 min using the same CMB suspension upon irradiation at 370 nm (Fig. 2c). The values were recorded when the irradiation was stopped. The first ZP value upon

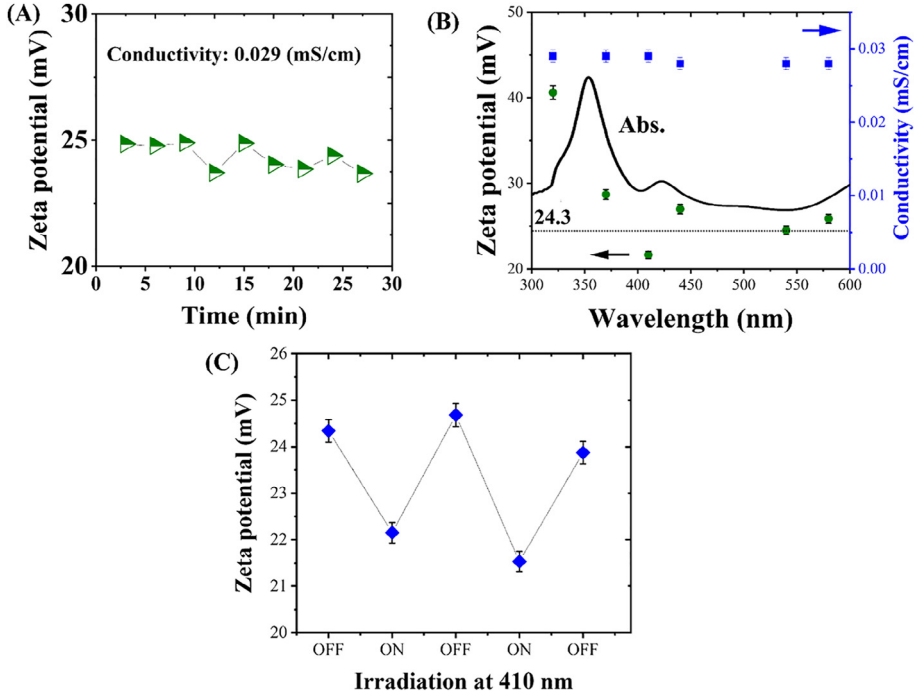

Fig. 3. A) ZP versus time excited at 370 nm and B) the dependence of the ZP and electric conductivity on the irradiation, C) the sensitivity of ZP during light irradiation at 410 nm of the TBH in acetone/water.

irradiation at 370 nm was about −42 mV and reached a peak of −47 mV after 40 min. The continual irradiation could keep the electrons in the excited state configuration.

The ZPs of TBH were continually recorded at about 24.3 ± 0.3 mV for 30 min without changing the electric conductivity of 0.029 mS/cm (Fig. 3a). This means that the chemical composition of TBH in a solvent is relatively stable without exchanging the apical ligand under an electric field created by a current of −0.6 mA. The absorption spectrum of TBH coupled with the ZP measured at the selected wavelength is illustrated in Fig. 3b. The conductivity remained at around 0.029 mS/cm when TBH was irradiated at different wavelengths. The average ZP was based on 5 measurements. In the case of TBH, the measurement was performed during the irradiation because TBH has no luminescent emission [11,16]. Due to the very low absorption around 540 nm, TBH maintained the same ZP as the non-irradiated sample which is reasonable. However, the positive ZP of TBH increases during irradiation at 370, 440, and 580 nm, following the extinction coefficient of the cluster. Very interestingly, the ZP is only reduced by about 2.7 mV when irradiating at 410 nm. Hence, the ZP was recorded in the same suspension with and without irradiation at 410 nm (Fig. 3c). After two cycles, ZP can repeat the non-irradiated value. This phenomenon was not observed at the other irradiation wavelengths. Based on this result, the electronic state on the charged surface of the $[\{Ta_6(\mu_2\text{-}Br)^i_{12}\}(H_2O)^a_6]^{2+}$ cluster during irradiation at 410 nm should be further investigated.

4. Conclusions

We report in this study the dependence of the zeta potential as a function of the light excitation wavelength for the $[\{Mo_6Br^i_8\}Br^a_6]^{2-}$ anionic cluster unit and the cationic $[\{Ta_6Br^i_{12}\}(H_2O)^a_6]^{4+}$ cluster units. With the existence of an electron in a valence band, the cluster can be oxidized during the excitation by light irradiation in the required range, which was observed by the change in the ZP of the charged particle surface in an electric field. Besides this essential suggestion, different possibilities relating to the change in the ligands of the MCs, geometrical relaxations, and size effect could be the origin of the changing zeta potential values. For the strong emitting $Cs_2\{Mo_6Br^i_8\}Br^a_6$ cluster, the photo-oxidation property also depends on the photoluminescence and the stability of the excited electron. Interestingly, for the $Br_2[\{Ta_6Br^i_{12}\}(H_2O)^a_6]$ octahedral cluster, the reversion of the ZP as well as the electronic state on the charged surface with and without irradiation at 410 nm appears to be a promising property for sensor applications. These preliminary results have highlighted the high potentials to generate an efficient photo-induced charge transfer based on these low-toxic, cheap, and stable M_6-based functional materials. These results will pave the way for extending the applicability of such cluster units in the fields of catalysis, optoelectronics and biologicals.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] F. Meinardi, F. Bruni, S. Brovelli, Nat. Rev. Mater. 2 (2017) 1–9.
[2] P.S. Kuttipillai, Y. Zhao, C.J. Traverse, R.J. Staples, B.G. Levine, R.R. Lunt, Adv. Mater. 28 (2016) 320–326.
[3] P.C. Ford, A. Vogler, Acc. Chem. Res. 26 (1993) 220–226.
[4] T.G. Gray, C.M. Rudzinski, E.E. Meyer, R.H. Holm, D.G. Nocera, J. Am. Chem. Soc. 125 (2003) 4755–4770.
[5] L.F. Szczepura, J.A. Edwards, D.L. Cedeno, J. Clust. Sci. 20 (2009) 105–112.
[6] N.G. Naumov, K.A. Brylev, Y.V. Mironov, S. Cordier, V.E. Fedorov, J. Struct. Chem. 55 (2014) 1371–1389.
[7] S. Cordier, F. Grasset, R. Boukherroub, N. Saito, H. Haneda, Y. Molard, S. Ravaine, M. Mortier, M. Amela-Cortes, N. Ohashi, J. Inorg, Organomet Polym. 25 (2015) 189–204.
[8] B. Dierre, K. Costuas, N. Dumait, S. Paofai, M. Amela- Cortes, Y. Molard, F. Grasset, Y. Cho, K. Takahashi, N. Ohashi, T. Uchikoshi, S. Cordier, Sci. Technol. Adv. Mater. 18 (2017) 458–466.
[9] S. Akagi, S. Fujii, N. Kitamura, Dalton Trans. 47 (2018) 1131–1139.
[10] S. Fujii, T. Horiguchi, S. Akagi, N. Kitamura, Inorg. Chem. 55 (2016) 10259–10266.
[11] A. Renaud, M. Wilmet, T.G. Truong, M. Seze, P. Lemoine, N. Dumait, W. Chen, N. Saito, T. Ohsawa, T. Uchikoshi, N. Ohashi, S. Cordier, F. Grasset, J. Mater. Chem. C 5 (2017) 8160–8168.
[12] M. Potel, C. Perrin, A. Perrin, M. Sergent, Mat. Res. Bull 21 (1986) 1239–1245.
[13] S. Cordier, Y. Molard, K.A. Brylev, Y.V. Mironov, F. Grasset, B. Fabre, N.G. Naumov, J. Clust. Sci. 26 (2015) 53–81.
[14] N.A. Vorotnikova, Y.A. Vorotnikov, I.N. Novozhilov, M.M. Syrokvashin, V.A. Nadolinny, N.V. Kuratieva, D.M. Benoit, Y.V. Mironov, R.I. Walton, G.J. Clarkson, N. Kitamura, A.J. Sutherland, M.A. Shestopalov, O.A. Efremova, Inorg. Chem. 57 (2018) 811–820.
[15] T.K.N. Nguyen, F. Grasset, B. Dierre, C. Matsunaga, S. Cordier, P. Lemoine, N. Ohashi, T. Uchikoshi, ECS J. Solid State Sci. Technol. 5 (2016) 178–186.
[16] T.K.N. Nguyen, A. Renaud, M. Wilmet, N. Dumait, S. Paofai, B. Dierre, W. Chen, N. Ohashi, S. Cordier, F. Grasset, T. Uchikoshi, J. Mater. Chem. C 5 (2017) 10477–10484.
[17] K. Kirakci, S. Cordier, C. Perrin, Z. Anorg, Allg. Chem. 631 (2005) 411–416.