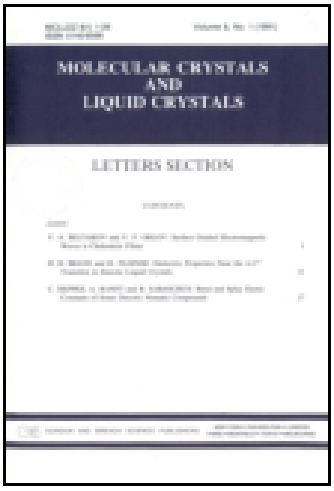

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Synthesis and Characterization of Fullerene-Metal Compound with Long Alkyl Chain for Liquid Crystals, Supramolecules, and Optoelectronic Materials

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*A novel C_{60}-Os_3 (carbon-metal) compound with long alkyl chain, $Os_3(CO)_8[(C_{16}H_{33}O)_3C_6H_2NC](\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{60})$ (**2**), was synthesized by substituted reaction between one CO of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{60})$ and $(C_{16}H_{33}O)_3C_6H_2NC$ (**1**). Compound **1** and **2** have been characterized by IR and ^1H NMR. Cyclic voltammetry (CV) and differential scanning calorimetry (DSC) were performed to electrochemical property and phase transition of **2**.*

Keywords Fullerene; metal cluster; long alkyl chain

Introduction

The C_{60} derivatives have been intensively studied due to potential application such as optical, magnetic, electronic, catalytic, and biological areas of material science [1, 2]. Especially, C_{60}-metal cluster compounds show strong electronic communication between C_{60} and metal centers that can be readily controlled by change of ligands attached to the metal center [3–5]. Therefore, the fullerene-metal compounds are useful for new electronic nanomaterials and nanodevices. Nakanishi group has been studied for supramolecules, nanomaterials, and their applications such as liquid crystals of long chain alkylated C_{60} derivatives [6–8].

Herein, I report the C_{60}-Os_3 (carbon-metal) compound with long alkyl chain, $Os_3(CO)_8[(C_{16}H_{33}O)_3C_6H_2NC](\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{60})$ (**2**), because it is thought that the C_{60}-metal compound combined long alkyl chain can lead to application of metal-carbon hybrid materials.

Experimental

General Comments. Solvents were dried over the appropriate drying agents and distilled immediately before use. Anhydrous trimethylamine *N*-oxide was obtained from

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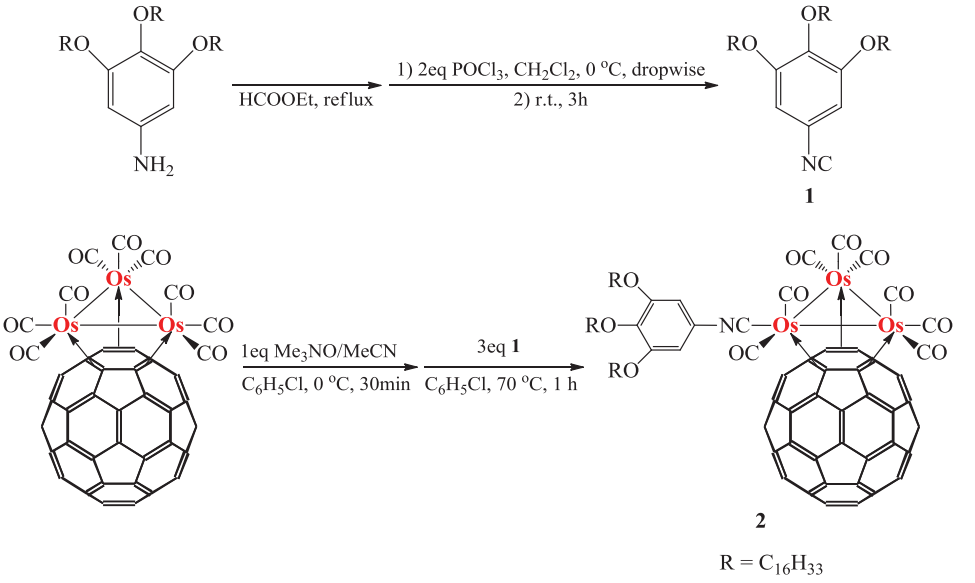
$Me_3NO{\cdot}2H_2O$ (98%, Aldrich) by sublimation (three times) at 90–100°C under vacuum. $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{60})$ [9] and 3,4,5-Trihexyloxyaniline [10] were prepared by the literature methods. Preparative thin layer plates were prepared with silica gel GF_{254} (Type 60, E. Merck).

Preparation of $(C_{16}H_{33}O)_3C_6H_2NC$ (1). 3,4,5-Trihexyloxyaniline (82.9 mg, 0.6 mmol) was refluxed in ethyl formate (30 mL) for 20 h. The solution was cooled and solvent was removed under reduced pressure. Triethylamine (10 mL) was added to solution of the residue in dry CH_2Cl_2 (30 mL). $POCl_3$ (0.057 mL, 0.6 mmol) was added dropwise to the mixture by syringe at 0°C under N_2. The dispersion mixture was warmed and stirred overnight at room temperature. The mixture was poured cold water (30 mL) and extract with CH_2Cl_2 (2 × 30 mL). The organic layer was washed with saturated aqueous $NaHCO_3$ solution and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and crude product was purified by column chromatography (CH_2Cl_2:Hexane = 7:3). The compound **1** as a white solid was further purified by recrystallization from CH_2Cl_2/Ethanol. Yield 64.0 mg, 72%; IR(CH_2Cl_2): ν_{NC} 2130 (s); ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 6.54 (s, 2H, aromatic), 3.92 (m, 6H, -CH_2O-), 1.74 (m, 6H, -CH_2CH$_2$O-), 1.45 (m, 6H, -CH_2CH$_2$CH$_2$O-), 1.24 (m, 72H, -(CH_2)$_{12}$-), 0.89 (t, J = 6.8Hz, 9H, CH_3).



Scheme 1. Synthesis of **1** and **2**.

Preparation of $Os_3(CO)_8[(C_{16}H_{33}O)_3C_6H_2NC](\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{60})$ (2). A chlorobenzene solution (30 mL) of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{60})$ (**1**, 30 mg, 0.0195 mmol) was cooled to 0°C, and an acetonitrile solution (3 mL) of anhydrous Me_3NO (1.47 mg, 0.0195 mmol) was dropwised. The reaction mixture was allowed to warm to room temperature for 30 min. After evaporation of the solvent in vacuo, the residue and **1** (8.9 mg, 0.060 mmol) were dissolved in chlorobenzene (30 mL). The reaction mixture was stirred at 70°C for 1 h. Evaporation of the solvent and purification by preparative TLC (CS_2:CH_2Cl_2 = 8:1) produced compound **2** as a brown solid. Yield 17.8 mg, 0.0076 mmol, 39%, R_f = 0.5; IR(CH_2Cl_2): ν_{NC} 2163 (m), ν_{CO} 2067 (vs), 2038 (vs), 2019 (s), 1998 (m), 1968 (sh) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 298K δ 6.47 (s, 2H, aromatic), 3.91 (t, J = 6.5Hz, 2H, -CH_2O-), 3.83

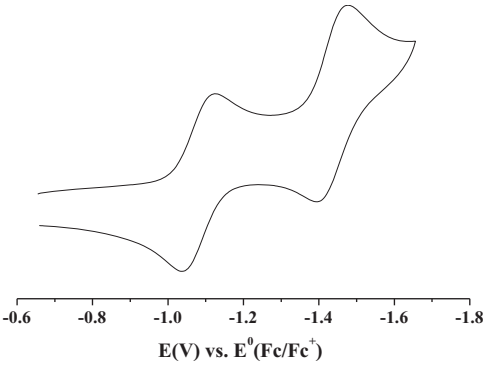


Figure 1. CV of **2** in chlorobenzene (scan rate = 50 mV/s).

(t, J = 6.6Hz, 4H, -CH_2O-), 1.71 (m, 6H, -CH_2CH_2O-), 1.40 (m, 6H, -CH_2CH_2CH_2O-), 1.24 (m, 72H, O-(CH_2)$_{12}$-), 0.86 (t, J = 6.5Hz, 9H, CH_3).

Results and Discussion

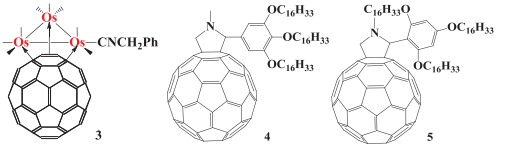
Compound **1** was synthesized from reaction of 3,4,5-trihexyloxyaniline with ethyl formate and $POCl_3$ (72%) (Scheme 1). Decarbonylation of $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ with 1.1 equiv. of Me_3NO/MeCN, followed by reaction with compound **1** in chlorobenzene (CB) at 70°C for 1 h, gave $Os_3(CO)_8[(C_{16}H_{33}O)_3C_6H_2NC](\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**2**) (39%) (Scheme 1).

IR spectra for NC triple bond of **1** and **2** show 2130 and 2163 cm^{-1}, respectively. Compound **2** exhibits strong ν(CO) stretches at 2067, 2038, 2019, 1998, and 1968 cm^{-1} which almost resemble IR frequency of $Os_3(CO)_8(L)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (L = isocyanide, phosphine).[3, 5] ^{1}H NMR spectra of **2** are similar to those of **1** except two splitting peaks (3.91 and 3.83 ppm) for methylene proton (-OCH_2-) of long alkyl chain.

Cyclic voltammetries (CV) of free C_{60}, $Os_3(CO)_8(CNCH_2Ph)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})$ (**3**), and **2** show two reversible one-electron redox couples with very similar half-wave potentials (Table 1, Figure 1). The results may be ascribed to the inductive effect of the metal carbonyl cluster addends on the stabilization of the C_{60}-localized LUMO.[3–5] However, half-wave potentials of organic C_{60} compounds combined long alkyl chain are shifted to more negative potentials by 113 and 107 mV for **4** and by 164 and 159 mV for **5** compared with those of free C_{60} (in CH_2Cl_2) (Table 1). In a wide potential range (~ -1.7 V), the CV was shown that

Table 1. Half-wave potentials ($E_{1/2}$ vs $E^\circ_{Fc/Fc+}$) of free C_{60}, **3**, **4**, **5**, and **6**

	$E_{1/2}^{0/-1}$	$E_{1/2}^{-1/-2}$	solvent	ref
C_{60}	-1.06	-1.43	CB	5
2	-1.07	-1.44	CB	here
3	-1.06	-1.42	CB	5
C_{60}	-1.032	-1.427	CH_2Cl_2	10,11
4	-1.145	-1.534	CH_2Cl_2	10
5	-1.196	-1.586	CH_2Cl_2	11



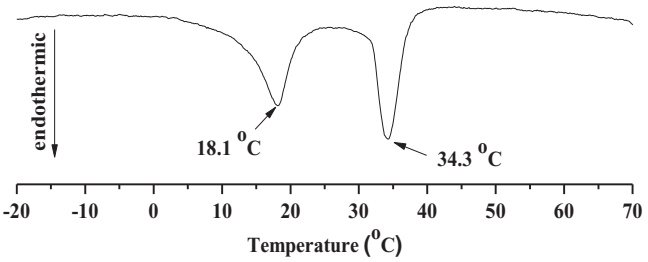


Figure 2. DSC thermogram of **2**.

the third redox wave was appeared to irreversible process. Therefore, **2** is electrochemically stable within −1.6 V.

The phase transition between crystalline and liquid crystalline phase of **2** was measured by differential scanning calorimetry (DSC). DSC data of **2** exhibits two endothermic peaks at 18.1°C (transition enthalpy, $\Delta H = 6.6$ kJ mol^{-1}; entropy, $\Delta S = 22.8$ J mol^{-1} K^{-1}) and 34.3°C (transition enthalpy, $\Delta H = 5.3$ kJ mol^{-1}; entropy, $\Delta S = 17.4$ J mol^{-1} K^{-1}).

Conclusion

C_{60}-Os_3 compound, $Os_3(CO)_8[(C_{16}H_{33}O)_3C_6H_2NC](\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{60})$ (**2**), substituted one long alkyl chain isocyanide ligand, $(C_{16}H_{33}O)_3C_6H_2NC$ (**1**), was synthesized and characterized. Electrochemical property of **2** is similar to that of C_{60}, while organic C_{60} compounds combined long alkyl chain **4** and **5** are needed to more negative potential to enter electron. Compound **2** is shown to possibility of application as liquid crystal by DSC. Also, supramolecules and nanomaterials are able to be form through assembly **2**.

References

[1] Bendikov, M., Wudl, F., & Perepichka, D. F. (2004). *Chem. Rev.*, *104*, 4891–4945.
[2] Nakamura, E., & Isobe, H. (2004). *Acc. Chem. Res.*, *36*, 807–815.
[3] Lee, K., Song, H., & Park, J. T. (2003). *Acc. Chem. Res.*, *36*, 78–86 and references therein.
[4] Park, B. K., Lee, G., Kim, K. H., Kang, H., Lee, C. Y., Miah, M. A., Jung, J., Han, Y.-K., & Park, J. T. (2006). *J. Am. Chem. Soc.*, *128*, 11160–11172 and references therein.
[5] Lee, C. Y., Park, B. K., Yoon, J. H., Hong, C. S., & Park, J. T. (2006). *Organometallics 25*, 4634–4642 and references therein.
[6] Li, H., Choi, J., & Nakanishi, T. (2013). *Langmuir*, *29*, 5394–5406 and references therein.
[7] Nakanishi, T., Miyashita, N., Michinobu, T., Wakayama, Y., Tsuruoka, T., Ariga, K., & Kurth, D. G. (2006). *J. Am. Chem. Soc.*, *128*, 6328–6329 and references therein.
[8] Michinobu, T., Nakanishi, T., Hill, J. P., Funahashi, M., & Ariga, K. (2006). *J. Am. Chem. Soc.*, *128*, 10384–10385 and references therein.
[9] Park, J. T., Song, H., Cho, J.-J., Chung, M.-K., Lee, J.-H., & Suh, I.-H. (1998). *Organometallics*, *17*, 227–236.
[10] Yelamaggad, C. V., Achalkumar, A. S., Rao, D. S. S., & Prasad, S. K. (2007). *J. Org. Chem.*, *72*, 8308–8318.
[11] Yagai, S., Usui, M., Seki, T., Murayama, H., Kikkawa, Y., Uemura, S., Karatsu, T., Kitamura, A., Asano, A., & Seki, S. (2012). *J. Am. Chem. Soc.*, *134*, 7983–7994.