Effective Derivatization and Extraction of Insoluble Missing Lanthanum Metallofullerenes La@C_{2n} (n=36-38) with Iodobenzene

Yutaka Maeda,^a Takayoshi Tsuchiya,^b Takashi Kikuchi,^b Hidefumi Nikawa,^b Tao Yang,^c Xiang Zhao,^{c,*} Zdenek Slanina,^b Mitsuaki Suzuki,^a Michio Yamada,^a Yongfu Lian,^d Shigeru Nagase,^e Xing Lu,^f Takeshi Akasaka^{a,b,f,g*}

^a Department of Chemistry, Tokyo Gakugei University, Koganei, Tokyo 184-8501, Japan

^b Life Center of Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan

^c Institute for Chemical Physics & Department of Chemistry, State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an 710049, China

^d Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China

^e Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto, 606-8103, Japan.

^f College of Materials Science and Engineering, Huazhong University of Science and Technology 430074 Wuhan, China

^g Foundation for Advancement of International Science, Tsukuba, Ibaraki 305-0821, Japan

*Corresponding author. Tel: +81-9032006305. E-mail: akasaka@tara.tsukuba.ac.jp

Abstract

Extraction of insoluble metallofullerenes, La@C_{2n} ($n = 36-38$), was conducted with dichlorobenzene, chlorobenzene, and iodobenzene as a solvent under reflux condition. When iodobenzene was used, La@C_{2n} ($n = 36-38$) was successfully extracted as the corresponding phenyl adducts, such as $\text{La@C}_{72}(\text{C}_6\text{H}_5)$, $\text{La@C}_{74}(\text{C}_6\text{H}_5)$, and $\text{La@C}_{76}(\text{C}_6\text{H}_5)$. The number of isomers of corresponding adducts, $\text{La@C}_{72}(\text{C}_6\text{H}_5)$ and $\text{La@C}_{74}(\text{C}_6\text{H}_5)$, were reduced to one-third of that in 1,2,4-trichlorobenzene-extracts, which was reported previously. Based on the spectroscopic analysis, the carbon cages of $\text{La@C}_{72}(\text{C}_6\text{H}_5)$ and $\text{La@C}_{74}(\text{C}_6\text{H}_5)$ were deduced to be $\text{La@C}_{2(10612)}\text{-C}_{72}(\text{C}_6\text{H}_5)$ and $\text{La@D}_{3h}\text{-C}_{74}(\text{C}_6\text{H}_5)$, respectively. The addition site carbon possessing very high radical character suggests that the corresponding adducts were produced by the addition of phenyl radical generated from iodobenzene on metallofullerenes.

1. Introduction

Endohedral metallofullerenes (EMFs) have attracted special attention because of their unique structures and electronic properties caused by the electron transfer from the encapsulated metals to the fullerene cage [1-3]. In 1991, Smalley and co-workers reported the production and the first solvent-extraction of lanthanum encapsulating EMFs [4]. Interestingly, molecular ion peaks attributed to LaC_{60} , LaC_{70} , and LaC_{74} were not detected in the mass spectrum of the toluene extract, although they were found in the mass spectrum of sublimed fullerenes. For a long time, it had been unclear why LaC_{60} , LaC_{70} , and LaC_{74} were not extracted. In 2005, La@C_{74} was extracted with 1,2,4-trichlorobenzene (TCB) under reflux condition as its corresponding dichlorophenyl adducts, $\text{La@C}_{74}(\text{C}_6\text{H}_3\text{Cl}_2)$ [5]. Three isomers of $\text{La@C}_{74}(\text{C}_6\text{H}_3\text{Cl}_2)$ were isolated and characterized. In 2011, additional three isomers of $\text{La@C}_{74}(\text{C}_6\text{H}_3\text{Cl}_2)$ were isolated and thus it was confirmed that two sets of regioisomers of $\text{La@C}_{74}(\text{C}_6\text{H}_3\text{Cl}_2)$ were produced under the TCB extraction [6]. Interestingly, according to the single crystal X-ray structure analysis and theoretical calculations, the carbon atoms at the site of dichlorophenyl addition on La@C_{74} have high spin density and high p-orbital axial vector (POAV) analysis values. Thus, the radical addition mechanism for the formation of $\text{La@C}_{74}(\text{C}_6\text{H}_3\text{Cl}_2)$ under extraction condition was proposed. The results give the answer why these fullerenes were not extractable in toluene under reflux condition. These fullerenes possessing high radical character should be trapped by reactive carbon species, such as amorphous carbon and metal carbide in the raw soot. Thus, inextractable reactive fullerenes can be stabilized by the addition of dichlorophenyl radical generated from TCB. As a result, the dichlorophenyl adducts have been extracted by increase of their solubility. In fact, $\text{La@D}_{3h}\text{-C}_{74}(\text{C}_6\text{H}_3\text{Cl}_2)$, $\text{La@C}_{2v}(3)\text{-C}_{80}(\text{C}_6\text{H}_3\text{Cl}_2)$, and $\text{La@C}_{3v}(7)\text{-C}_{82}(\text{C}_6\text{H}_3\text{Cl}_2)$, were isolated and characterized by the single-crystal X-ray diffraction (XRD) crystallographic

analyses [7-9]. Theoretical calculations showed that the carbon atoms at the sites of addition on these fullerenes always possess very high radical character. Therefore, the TCB extraction is potentially useful for the investigation on other inextractable metallofullerenes, such as metal encapsulated C_{60} . However, TCB is not a suitable radical precursor because three regioisomers, 2,4-, 2,5-, and 3,4-dichlorophenyl radicals, are potentially generated by the cleavage of a carbon-chloride bond. In fact, 2,4-, 2,5-, and 3,4-dichlorophenyl derivatives, $La@C_n(C_6H_3Cl_2)$ -A, -B, and -C, whose addition positions on the fullerene cage carbons are the same, were obtained from TCB-extracts (Scheme 1). In this context, a radical precursor producing only one isomer on each addition position is desired for effective isolation and characterization of inextractable fullerenes via exohedral derivatization (Scheme 2). In this study, we investigate the stabilization and extraction of highly reactive lanthanum encapsulated fullerenes by using dichlorobenzene, chlorobenzene, and iodobenzene. In addition, isolation and characterization of phenyl derivatives, $La@C_{2n}(C_6H_5)$ ($n=36-38$), were conducted.

2. Experimental

2.1 General

High performance liquid chromatograph (HPLC) was performed using chromatographs (LC-9201 and LC-918; Japan Analytical Industry Co. Ltd.) that were monitored using UV absorption at 330 nm. 1H and ^{13}C NMR measurements were conducted on spectrometers (Bruker AVANCE-500; Bruker Biospin K.K.) with CryoProbe system (Bruker Analytik GmbH). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy was performed (Bruker BIFLEX III; Bruker Daltonics Inc.) with 1,1,4,4-tetraphenyl-1,3-butadiene as the matrix. The absorption spectra were measured using spectrophotometer (UV-3150; Shimadzu

Corp.). Differential pulse voltammogram (DPVs) were recorded on electrochemical analyzer (CV50W; BAS Inc.) containing 0.1 M (*n*Bu)₄NPF₆ in 1,2-dichlorobenzene. Platinum wires were used as the working electrode and the counter electrode. The reference electrode was a saturated calomel reference electrode (SCE). All potentials were referenced to the ferrocene/ferrocenium couple (Fc/Fc⁺) as the standard. Condition of DPV: pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mVs⁻¹.

2.2 Synthesis and isolation of metallofullerene

Soot-containing metallofullerenes were produced by DC (256 A, 35 V) arc discharge with composite rods containing graphite and lanthanum oxide (atomic ratio of La/C is 2.0%) under a 150 Torr He atmosphere. 1 g of the raw soot was heated to reflux in 30 ml of 1,2,4-trichlorobenzene, 1,2-dichlorobenzene, chlorobenzene, or iodobenzene for 15 h, respectively, to extract fullerenes. The extract was filtrated and the residue was washed with a 10 ml of solvent. The extraction ratio of C₆₀ and La@C_{2v}-C₈₂ between each solvent (relative extraction efficiency) was estimated by using HPLC analysis with a preparative 5PYE column. The soluble fraction was separated by multi-stage HPLC with toluene as an eluent to obtain La@C_{2n}(C₆H₅) (n=36-38).

La@C₇₂(C₆H₅): ¹H NMR (500 MHz, CS₂/acetone-*d*₆ (capillary)) δ 7.60-7.54 (m, 2H), 6.99-6.93 (m, 2H), 6.83-6.78 (m, 1H); ¹³C NMR (125 MHz, CS₂/acetone-*d*₆ (capillary)) δ 155.37, 154.93, 152.83, 151.62, 151.34, 151.04, 150.75, 150.66, 150.21, 150.02, 149.75, 149.41, 149.05, 148.21, 148.06, 147.91, 147.84, 147.76, 147.47, 147.24, 146.40, 146.12, 145.72, 145.64, 145.54, 145.24, 144.92, 144.76, 144.46, 144.04, 143.17, 143.02, 142.65, 142.03, 141.95, 140.49, 140.44, 139.81, 139.37, 139.08, 138.85, 138.78, 138.48, 137.79, 137.20, 136.99, 136.13, 136.04, 135.52, 135.44, 134.60, 133.85, 133.66, 133.35, 132.14, 130.49, 130.37, 130.24, 130.04, 129.53, 129.31, 129.27, 129.22, 129.08, 128.93, 128.75, 128.61, 128.39, 128.20, 128.14, 126.78, 125.82, 124.27, 101.27, 100.06, 58.06; UV-vis-NIR (in CS₂) λ_{max} 552, 662, 951, 1069;

LD-TOF mass (positive): m/z 1003 (La@C₇₂); MALDI-TOF mass (positive, matrix: 1,1,4,4-tetraphenyl-1,3-butadiene): m/z 1080 (La@C₇₂(C₆H₅)).

La@C₇₄(C₆H₅)-I: ¹H NMR (500 MHz, CS₂/acetone-*d*₆ (capillary)) δ 7.59-7.56 (m, 2H), 6.86-6.81 (m, 2H), 6.73-6.69 (m, 1H); ¹³C NMR (125 MHz, CS₂/acetone-*d*₆ (capillary)) δ 156.63, 154.85, 154.33, 151.95, 151.21, 151.08, 149.43, 148.90, 148.86, 148.50, 148.04, 147.73, 146.95, 146.49, 146.29, 146.18, 146.13, 145.56, 145.00, 144.36, 143.71, 143.65, 143.42, 143.23, 143.08, 142.94, 142.73, 141.98, 141.77, 141.70, 141.59, 141.49, 140.98, 140.81, 140.54, 139.96, 139.88, 139.24, 139.16, 138.92, 138.70, 138.51, 138.18, 137.51, 137.44, 136.74, 136.48, 135.72, 135.53, 134.95, 134.82, 134.75, 134.58, 134.32, 134.09, 133.23, 133.04, 131.42, 130.61, 129.80, 129.19, 128.39, 127.16, 126.73, 126.55, 126.49, 126.41, 117.15, 89.35, 51.62 (66 resonances out of 74 expected for fullerene cages due to peak overlap); UV-vis-NIR (in CS₂) $\lambda_{\max}$ 555, 742; LD-TOF mass (positive): m/z 1027 (La@C₇₄); MALDI-TOF mass (positive, matrix: 1,1,4,4-tetraphenyl-1,3-butadiene): m/z 1104 (La@C₇₄(C₆H₅)).

La@C₇₄(C₆H₅)-II: ¹H NMR (500 MHz, CS₂/acetone-*d*₆ (capillary)) δ 7.31-7.27 (m, 2H), 6.80-6.75 (m, 2H), 6.68-6.63 (m, 1H); ¹³C NMR (125 MHz, CS₂/acetone-*d*₆ (capillary)) δ 155.66, 155.02, 152.16, 150.72, 150.14, 149.64, 149.43, 148.88, 148.75, 147.47, 147.37, 147.09, 146.92, 146.66, 146.19, 146.12, 145.57, 145.52, 145.27, 144.94, 144.83, 144.17, 143.14, 143.06, 142.41, 142.36, 142.25, 141.64, 141.43, 141.30, 140.94, 140.62, 140.54, 139.84, 139.64, 139.20, 138.96, 138.58, 138.40, 138.23, 137.61, 137.37, 137.30, 137.21, 137.00, 136.67, 136.10, 135.68, 135.63, 135.41, 134.03, 133.96, 132.91, 132.84, 132.69, 132.43, 131.66, 130.76, 130.63, 129.92, 129.84, 129.29, 129.13, 128.85, 128.74, 127.17, 125.93, 125.73, 125.09, 98.92, 61.52 (67 resonances out of 74 expected for fullerene cages due to peak overlap); UV-vis-NIR (in CS₂) $\lambda_{\max}$ 511, 636, 759, 955, 1456; LD-TOF mass (positive): m/z 1027 (La@C₇₄); MALDI-TOF mass (positive, matrix: 1,1,4,4-tetraphenyl-1,3-butadiene): m/z 1104 (La@C₇₄(C₆H₅)).

La@C₇₆(C₆H₅)-I: ¹H NMR (500 MHz, CS₂/acetone-*d*₆ (capillary)) δ 7.63-7.56 (m, 2H), 6.94-6.86 (m, 2H), 6.80-6.74 (m, *J* = 7.4 Hz, 1H); ¹³C NMR (125 MHz, CS₂/acetone-*d*₆ (capillary)) δ 155.56, 153.18, 151.51, 150.98, 150.82, 149.97, 149.00, 148.68, 148.54, 147.81, 147.65, 147.25, 146.97, 146.56, 146.37, 145.82, 145.77, 145.62, 145.02, 144.94, 144.09, 143.61, 141.08, 140.84, 140.53, 140.44, 140.29, 140.22, 139.78, 139.69, 139.22, 138.94, 138.71, 138.40, 138.27, 138.25, 138.16, 137.97, 137.91, 137.82, 137.74, 137.67, 137.66, 137.32, 137.24, 137.14, 137.11, 137.01, 136.75, 136.26, 135.87, 135.74, 134.93, 134.28, 134.26, 130.82, 130.30, 129.63, 128.83, 128.38, 128.12, 127.70, 127.68, 127.62, 127.45, 127.33, 127.28, 91.94 (65 resonances out of 76 expected for fullerene cages due to peak overlap); UV-vis-NIR (in CS₂) λ_{max} 553, 640, 829; LD-TOF mass (positive): *m/z* 1051 (La@C₇₆); MALDI-TOF mass (positive, matrix: 1,1,4,4-tetraphenyl-1,3-butadiene): *m/z* 1128 (La@C₇₆(C₆H₅)).

La@C₇₆(C₆H₅)-II: ¹H NMR (500 MHz, CS₂/acetone-*d*₆ (capillary)) δ 7.69-7.64 (m, 2H), 6.99-6.93 (m, 2H), 6.81-6.75 (m, 1H); ¹³C NMR (125 MHz, CS₂/acetone-*d*₆ (capillary)) δ 161.80, 154.82, 152.84, 152.65, 152.26, 150.67, 150.00, 149.84, 149.15, 149.09, 149.03, 148.42, 148.05, 147.88, 147.40, 147.01, 146.94, 146.61, 146.56, 146.48, 145.96, 145.78, 145.72, 145.61, 145.54, 144.74, 144.46, 144.34, 143.89, 143.41, 143.29, 143.21, 142.58, 142.39, 142.21, 142.11, 142.01, 141.91, 141.77, 141.70, 140.86, 140.69, 139.77, 139.66, 138.20, 138.09, 137.67, 136.63, 136.57, 136.38, 135.87, 135.50, 135.42, 135.35, 135.28, 134.87, 133.51, 133.23, 133.16, 132.56, 131.95, 131.44, 131.25, 130.48, 130.25, 130.06, 129.63, 129.17, 129.05, 128.47, 127.74, 127.55, 126.49, 122.55, 117.16, 94.02, 68.19 (73 resonances out of 76 expected for fullerene cages due to peak overlap); UV-vis-NIR (in CS₂) λ_{max} 568, 670, 824, 989, 1398; LD-TOF mass (positive): *m/z* 1051 (La@C₇₆); MALDI-TOF mass (positive, matrix: 1,1,4,4-tetraphenyl-1,3-butadiene): *m/z* 1128 (La@C₇₆(C₆H₅)).

3. Results and Discussion

In the previous reports, 1,2,4-trichlorobenzene was used for extraction of $\text{La}@\text{C}_{2n}(\text{C}_6\text{H}_3\text{Cl}_2)$ ($n=36, 37, 40, 41$) [6-9]. To reduce the number of possible isomers depending on the substituent, 1,2-dichlorobenzene, chlorobenzene, or iodobenzene was used as an alternative solvent for the extraction of fullerenes. The extraction of fullerenes was carried out under reflux for 15 hours and the extracts were analyzed by HPLC with a 5PYE column (Fig. 1). Firstly, the relative extraction efficiency of soluble fullerenes was estimated from the relative HPLC peak area of C_{60} and $\text{La}@\text{C}_{2v}\text{-C}_{82}$ in the extracts using various solvents, as shown in Table 1. The relative HPLC peak area of both C_{60} and $\text{La}@\text{C}_{2v}\text{-C}_{82}$ decreased with the decrease in the boiling point of the solvent. Corresponding molecular ion peaks attributed to chlorophenyl- or phenyl-appended $\text{La}@\text{C}_{72}$ and $\text{La}@\text{C}_{74}$ were detected by MALDI-TOF mass analysis when dichlorobenzene or iodobenzene was used as an extraction solvent. In contrast, the formation of the corresponding adducts were not observed when chlorobenzene was used. The results suggest that iodobenzene is the most effective reagent to extract $\text{La}@\text{C}_{72}$ and $\text{La}@\text{C}_{74}$, as its derivatives because extraction efficiency of iodobenzene is high and the corresponding adducts were detected when iodobenzene is used (Fig. S1).

As shown in Fig. S1, single isomer of $\text{La}@\text{C}_{72}(\text{C}_6\text{H}_5)$ and two isomers of $\text{La}@\text{C}_{74}(\text{C}_6\text{H}_5)$ and $\text{La}@\text{C}_{76}(\text{C}_6\text{H}_5)$ were isolated by multi-step HPLC separation of iodobenzene extract (Fig. S3-5). Isolated adducts, $\text{La}@\text{C}_{72}(\text{C}_6\text{H}_5)$, $\text{La}@\text{C}_{74}(\text{C}_6\text{H}_5)\text{-I}$, $\text{La}@\text{C}_{74}(\text{C}_6\text{H}_5)\text{-II}$, $\text{La}@\text{C}_{76}(\text{C}_6\text{H}_5)\text{-I}$, and $\text{La}@\text{C}_{76}(\text{C}_6\text{H}_5)\text{-II}$, showed molecular ion peaks at m/z 1080, 1104, and 1128 respectively by MALDI-TOF mass analysis (Fig. 2). In order to determine the molecular structures of these adducts, ^1H NMR, ^{13}C NMR, and 2D NMR (HMQC and HMBC) measurements were performed. ^1H NMR spectra of these adducts showed *p*-, *m*-, and *o*-protons in the phenyl group (Fig. S7). ^{13}C NMR spectra of $\text{La}@\text{C}_{72}(\text{C}_6\text{H}_5)$ show total of 76 lines (Fig. 3). Four lines are assigned to phenyl

groups and the rest signals are assigned to the fullerene cages. *p*-, *m*-, and *o*-protons and carbons in the phenyl group were fully characterized based on their HMQC and HMBC spectra, as shown in Fig. S8. Accordingly, NMR results indicate that La@C₇₂(C₆H₅) has C₁ symmetry. Similarly, phenyl groups in La@C₇₄(C₆H₅)-I, La@C₇₄(C₆H₅)-II, La@C₇₆(C₆H₅)-I, and La@C₇₆(C₆H₅)-II were characterized based on their NMR spectra, as shown in Fig. S10-S14. ¹³C NMR spectra of La@C₇₄(C₆H₅)-I, La@C₇₄(C₆H₅)-II, La@C₇₆(C₆H₅)-I, and La@C₇₆(C₆H₅)-II show 66, 67, 65, and 73 signals assigned to the fullerene cage. Thus, the respective NMR data indicate these fullerene adducts also have C₁ symmetry, respectively.

It has been widely accepted that the absorption spectra of fullerene adducts reflect sensitively the cage structure and the addition position rather than the nature of the addends [6,9-14]. In fact, the respective three regioisomers of La@C₇₂(C₆H₃Cl₂)-I, La@C₇₄(C₆H₃Cl₂)-I, and La@C₇₄(C₆H₃Cl₂)-II show similar features in their absorption spectra, respectively. Interestingly, the absorption spectra of La@C₇₂(C₆H₅) show similar features to those previously reported for dichlorophenyl derivatives, La@C₇₂(C₆H₃Cl₂)-IA, La@C₇₂(C₆H₃Cl₂)-IB, and La@C₇₂(C₆H₃Cl₂)-IC (Fig. 4) [7]. In addition, La@C₇₄(C₆H₅)-I and La@C₇₄(C₆H₅)-II show the similar features to those previously reported for dichlorophenyl derivatives, La@C₇₄(C₆H₃Cl₂)-I(A-C) and La@C₇₄(C₆H₃Cl₂)-II(A-C) in the absorption spectra [6]. Thus, it is assumed that the addition position of the phenyl groups on La@C₇₂ or La@C₇₄ are identical to the dichlorophenyl derivatives formed by TCB extraction. Noted that the molecular structures of La@C₇₂(C₆H₃Cl₂) and La@C₇₄(C₆H₃Cl₂) were clarified by the XRD crystallographic analysis (5-7). Based on the spectroscopic analysis and molecular structures of the dichlorophenyl derivatives, the plausible structures and the addition position of the phenyl groups are shown in Fig. 5. The results also

support the radical addition mechanism for the formation of the phenyl adducts, as found in the dichlorophenyl addition of La@C₇₂ and La@C₇₄.

In 2001, pristine La@C₇₆ was extracted using CS₂ and pyridine and characterized using mass, absorption, and ESR spectra by Okubo et al [15], whereas the structure determination of La@C₇₆ was not achieved. In this study, extraction of La@C₇₆ in TCB was conducted and the corresponding adduct, La@C₇₆(C₆H₃Cl₂), has been successfully isolated (Fig. S15-17). Since La@C₇₆(C₆H₅)-I and La@C₇₆(C₆H₃Cl₂) show similar absorption spectra, it is estimated that these adducts have same fullerene cage (Fig. 6). Moreover, the isolation of two isomers of La@C₇₆(C₆H₅) in enough amount for NMR measurements should be results of the higher regioselectivity of iodobenzene than that of TCB. For the structure elucidation of La@C₇₆ and its phenyl adducts, further studies such as a single crystal X-ray structure analysis are required.

In order to clarify the electrochemical properties of the phenyl derivatives, DPV measurements of La@C₇₂(C₆H₅) were performed (Fig. 7). The oxidation and reduction potentials of La@C₇₂(C₆H₅) are shifted to more cathodic potentials in comparison with those of La@C₇₂(C₆H₃Cl₂), as shown in Table 2 [7]. This can be explained by the electron-withdrawing character of chloride atoms in the phenyl group.

4. Conclusion

We have examined the extraction of high-reactive lanthanum encapsulated fullerenes using dichlorobenzene, chlorobenzene, or iodobenzene under reflux condition. The extraction efficiency of C₆₀ and La@C₈₂ showed good relation with the boiling point of the solvent. When iodobenzene was used for the extraction of fullerenes, reactive fullerenes were extracted as the corresponding phenyl adducts, such as La@C₇₂(C₆H₅), La@C₇₄(C₆H₅), and La@C₇₆(C₆H₅).

Furthermore, the number of isomers of corresponding adducts, $\text{La}@C_{72}(\text{C}_6\text{H}_5)$ and $\text{La}@C_{74}(\text{C}_6\text{H}_5)$, was reduced to one-third of that in TCB-extracts. Based on the spectroscopic analysis, the carbon cages of $\text{La}@C_{72}(\text{C}_6\text{H}_5)$ and $\text{La}@C_{74}(\text{C}_6\text{H}_5)$ were deduced to be $\text{La}@C_{2(10612)}-C_{72}(\text{C}_6\text{H}_5)$ and $\text{La}@D_{3h}-C_{74}(\text{C}_6\text{H}_5)$, respectively. The stabilization and extraction of highly reactive fullerenes using iodobenzene is applicable to finding insoluble and unknown fullerenes still remained in raw soot.

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Fig. 1. HPLC profiles for fullerenes extracted in 1,2,4-trichlorobenzene, iodobenzene, 1,2-dichlorobenzene, and chlorobenzene under reflux condition for 15 h.

La@C₇₂(C₆H₅)-I

La@C₇₄(C₆H₅)-I

La@C₇₄(C₆H₅)-II

La@C₇₆(C₆H₅)-I

La@C₇₆(C₆H₅)-II

Fig. 2. MALDI-TOF mass spectra of La@C₇₂(C₆H₅), La@C₇₄(C₆H₅)-I, La@C₇₄(C₆H₅)-II, La@C₇₆(C₆H₅)-I, and La@C₇₆(C₆H₅)-II.

Fig. 3. ^{13}C NMR of $\text{La@C}_{72}(\text{C}_6\text{H}_5)$.

Fig. 4. Vis-NIR spectra of $\text{La@C}_{72}(\text{C}_6\text{H}_5)$, $\text{La@C}_{72}(\text{C}_6\text{H}_3\text{Cl}_2)$, $\text{La@C}_{74}(\text{C}_6\text{H}_5)$, and $\text{La@C}_{74}(\text{C}_6\text{H}_3\text{Cl}_2)$ in CS_2 . A: 2,4-dichlorophenyl derivatives. B: 2,5-dichlorophenyl derivatives. C: 3,4-dichlorophenyl derivatives.

Fig. 5. Plausible fullerene structures and addition positions of phenyl groups for $\text{La@C}_{72}(\text{C}_6\text{H}_5)$ and $\text{La@C}_{74}(\text{C}_6\text{H}_5)$ -I and -II.

Fig. 6. Vis-NIR spectra of La@C₇₆(C₆H₅)-I, La@C₇₆(C₆H₅), and La@C₇₆(C₆H₃Cl₂) in CS₂.

Fig. 7. DPV of La@C₇₂(C₆H₅).

Table 1. Relative extraction efficiency of C_{60} and $La@C_{2v}-C_{82}$ in 1,2,4-trichlorobenzene, iodobenzene, 1,2-dichlorobenzene, and chlorobenzene.

Solvent	bp (°C)	Relative extraction efficiency	
		C_{60}	$La@C_{2v}-C_{82}$
1,2,4-trichlorobenzene	214	1.00	1.00
iodobenzene	189	0.75	0.75
1,2-dichlorobenzene	181	0.41	0.09
chlorobenzene	132	0.17	0.01

Table 2. Redox potentials of $La@C_{72}(C_6H_5)$ and $La@C_{72}(C_6H_3Cl_2)$. A: 2,4-dichlorophenyl derivatives. B: 2,5-dichlorophenyl derivatives. C: 3,4-dichlorophenyl derivatives. Values were obtained by DPV.

Compounds	$^{ox}E_1$	$^{red}E_1$	$^{red}E_2$	$^{red}E_3$
$La@C_{72}(C_6H_5)$	0.35	-1.12	-1.52	-2.01
$La@C_{72}(C_6H_3Cl_2)-A^{(7)}$	0.44	-1.00	-1.37	-1.64
$La@C_{72}(C_6H_3Cl_2)-B^{(7)}$	0.42	-1.00	-1.36	-1.64
$La@C_{72}(C_6H_3Cl_2)-C^{(7)}$	0.46	-0.95	-1.29	-1.70

Scheme 1.

Scheme 2.