Organic &
Biomolecular
Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 6417

www.rsc.org/obc

PAPER

Facile fullerene modification: $FeCl_3$-mediated quantitative conversion of C_{60} to polyarylated fullerenes containing pentaaryl(chloro)[60]fullerenes†‡

Masahiko Hashiguchi,*[a] Kazuhiro Watanabe[a] and Yutaka Matsuo*[b]

Received 4th June 2011, Accepted 17th June 2011
DOI: 10.1039/c1ob05895a

A facile, one-step reaction using inexpensive reagents has been developed for functionalization of [60]fullerene, where the reaction of C_{60} with $FeCl_3$ in chlorobenzene proceeded at 25 °C with 100% conversion, yielding a mixture of polyarylated products containing pentaaryl(chloro)[60]fullerene, $C_{60}(C_6H_4Cl)_5Cl$ (up to 29%) and other polyarylated fullerenes (number of aryl groups is in a range from 5 to 10).

Introduction

Development of a simple and low-cost procedure for producing fullerene derivatives is important for their commercial production. Although several low-cost methods for production[1] and purification[2] of parent fullerenes have been developed to date, there has been little research into the economical synthesis of fullerene derivatives.[3] The most costly process for production of fullerene derivatives is generally isolation and purification of the target compound from a product mixture containing multi-adducts. However, in some cases for industrial-scale processes, an inexpensive product mixture itself is also important. For instance, product mixtures such as polyarylated fullerene ($C_{60}Ar_nR_2$; n = 8 and 10; R = H and alkyl groups), polyhydroxylated fullerene ($C_{60}(OH)_n$; n > 8), polyaminated fullerenes, and mixture of bis-PCBMs have been utilized to photoresist materials for extreme-UV lithography,[4] proton conductors for fuel cells,[5] optical limiting materials,[6] and electron-acceptors in organic photovoltaic cells.[7] On these applications, chemical modification is a tool to tune the electronic properties and solubility of fullerene derivatives mixtures. As functional polymers with polydispersities have been used generally, fullerene derivative mixtures have been also employed as functional materials. Note that such inexpensive modified fullerenes mixtures have been often adopted, rather than expensive single products in industry.

Among fullerene derivatives, arylated[60]fullerenes are interesting materials not only in organic chemistry but also in nanoscale materials science. Penta(aryl)[60]fullerenes, in particular, have shown many fascinating physical and chemical properties as reported by Nakamura and coworkers.[8] However, expensive organometallic reagents (*i.e.*, Grignard reagents) are normally used in the arylation of C_{60};[9] therefore, this synthetic method has still held a drawback for industrial large-scale applications. On the other hand, Friedel–Crafts arylation reactions of fullerenes using Lewis acids have been reported since 1990s.[10] Although the $AlCl_3$-mediated Friedel–Crafts reaction is the simplest method for the synthesis of arylated fullerene derivatives, it is difficult to introduce only aryl groups to the C_{60} core because hydrogenation also proceeds in parallel with arylation.[10] The use of inexpensive $FeCl_3$ for the Friedel–Crafts reactions in the presence of bromine has been also attempted.[11] In this investigation toluene and xylene were used as substrates, but products characterization was not sufficient likely because of severely complex mixtures of the products. The most problematic thing is a remaining C_{60}, which tends to block a way to the purpose.

Herein we report a new class of method, that is, inexpensive $FeCl_3$-mediated polyarylation of C_{60} by using aryl halides with a facile synthetic procedure. The reaction of C_{60} with chlorobenzene in the presence of $FeCl_3$ yielded a mixture of arylated products (5 ≤ number of aryl groups ≤ 10) containing penta(aryl)[60]fullerenes up to 29% yield (Scheme 1). Although the product is a mixture, the conversion of C_{60} is almost quantitative. This convenient fullerene-modification method will produce industrially useful materials at low cost.

Results and discussion

The main advantage of the present reaction is a facile and inexpensive procedure as well as almost quantitative conversion

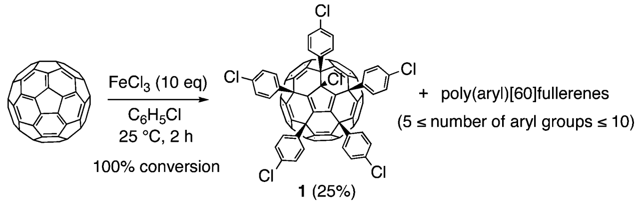
---

[a] *Fullerene Development Group, Performance Products Division, Mitsubishi Chemical Corporation, 1-1 Kurosakishiroishi, Yahatanishi-ku, Kitakyushu, 806-0004, Japan. E-mail: 6206530@cc.m-kagaku.co.jp; Fax: +81-93-643-4401*

[b] *Department of Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan. E-mail: matsuo@chem.s.u-tokyo.ac.jp; Fax: +81-3-5841-1476; Tel: +81-3-5841-1476*

† Electronic supplementary information (ESI) available: Synthetic procedures, HPLC Charts, and X-ray crystallographic spectra. For ESI and CIF of **1**·($C_6H_5CH_3$). CCDC reference number 804404. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ob05895a

‡ We thank Prof. Eiichi Nakamura for technical consultation. We are also grateful to the Mitsubishi Chemical Science and Technology Research Center, Inc. for useful suggestions and discussion. This research is partially supported by the Japan Society for the Promotion of Science (JSPS) through its "Funding Program for Next Generation World-Leading Researchers".



Scheme 1 Inexpensive functionalization of C_{60} with $FeCl_3$ and aryl halides.

of fullerene. A mixture of [60]fullerene (501 mg) and $FeCl_3$ (1.13 g, 10.0 equiv) in chlorobenzene (25 mL) was stirred at 25 °C for 2 h, yielding a mixture of products containing the pentaadduct $C_{60}(C_6H_4Cl)_5Cl$ (**1**) and various other polyarylated fullerene derivatives. Fig. 1 shows an HPLC trace for this product mixture: a peak at the retention time of 14.5 min was assigned to compound **1** by its characteristic UV-vis spectrum.[9e] Compounds with retention time less than about 14 min in Fig. 1 are polyarylated products (number of aryl groups > 5). Notably, there is no peak for the starting material C_{60} (retention time = *ca.* 18 min). Atmospheric pressure photoionization mass spectrometry (APPI-MS) revealed the existence of compound **1**, as well as hepta-, octa-, and deca-adducts.[12] This reaction represents an inexpensive 100%-conversion reaction that can provide a polyarylated fullerene mixture. Although this is the purpose of the research, we did separation of **1** for structural characterization and further discussion. Preparative HPLC separation of **1** from the product mixture using a Cosmosil Buckyprep column (Nacalai Tesque) afforded pure compound **1** in 25% isolated yield (Table 1, entry 1). Pure product **1** was characterized by ^{1}H and ^{13}C NMR and combustion analysis. The structure of **1** was determined unambiguously by X-ray crystallographic analysis (Fig. 2) of a single crystal, obtained by slow diffusion of methanol into a solution of **1** in toluene. The chlorine atom is accommodated in the space surrounded by five aryl groups. Because of positional disorder of the chlorine atom on the five-membered ring of the cyclopentadiene moiety, we were not able to discuss the bond length between the chlorine and carbon atoms.

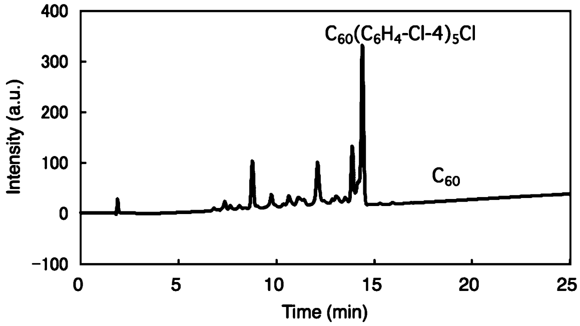


Fig. 1 HPLC trace for the product mixture containing **1**. Peaks at the retention time less than about 14 min represent multiple-adducts bearing more than five aryl groups. Conditions: YMC-Pack ODS-AM, 5 micron, 4.6 × 150 mm. Linear methanol/toluene gradient from 25% to 55% toluene over 25 min; flow rate: 1.0 mL/min.

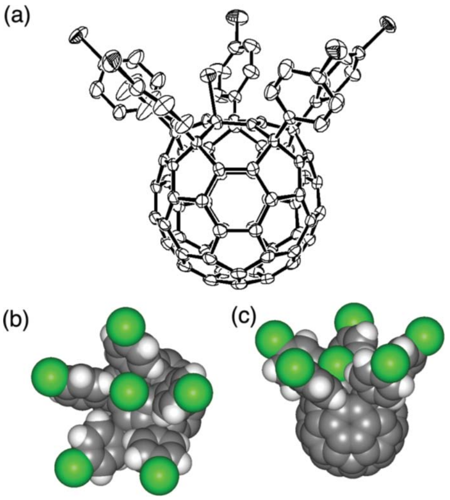


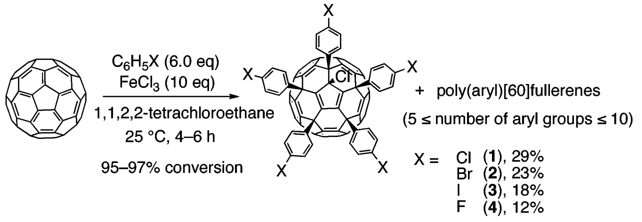
Fig. 2 Crystal structure of $\mathbf{1}\cdot(C_6H_5CH_3)$. (a) ORTEP drawing with thermal ellipsoids at 30% probability. Solvent molecules found in the unit cell and disordered chlorine atoms are omitted for clarity. (b), (c) Space-filling models.

We next investigated the scope and limitations of this reaction. When toluene, *p*-xylene, 1,2,4-trimethylbenzene, or anisole were used in place of chlorobenzene, the reaction proceeded slowly to afford trace amounts of hydroarylated products and remaining C_{60} (*ca.* 30%, see ESI†).[10b] Other Lewis acids were tested; $FeCl_2$, $FeBr_3$, $ZnCl_2$, $AlCl_3$, $BF_3\cdot Et_2O$, $RuCl_3$, $CeCl_3\cdot 7H_2O$, $TiCl_4$, $NiCl_2$, and $CoCl_2$ all gave poor results. Only $FeBr_3$ gave 10% conversion of C_{60}, but the product was a complex mixture of unidentifiable products. Hence, we found this reaction system only works with halogenated benzenes and $FeCl_3$. We surmise that not only Lewis acidity but also strong electron accepting ability to oxidize the fullerene part is necessary for this reaction (*vide infra*).

We then focused on reaction systems using different organic solvents (Scheme 2). The amount of chlorobenzene was reduced from solvent scale to 6 molar equivalents with respect to C_{60}. The use of chlorinated solvents such as CH_2Cl_2, $CHCl_3$, and 1,1,2,2-tetrachloroethane gave good C_{60} conversion (Table 1, entries 2–4). In particular, 1,1,2,2-tetrachloroethane was a preferred solvent, because it dissolves C_{60} and does not have an aromatic moiety

Table 1 $FeCl_3$-mediated multiarylation reaction of C_{60}

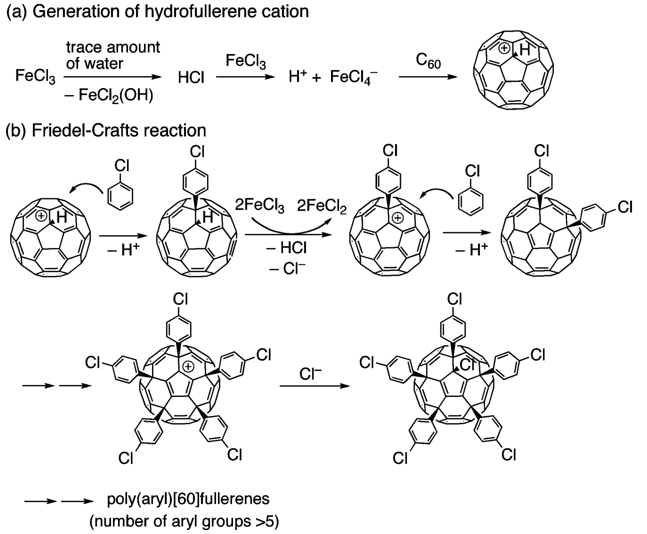
Entry	Substrate	Solvent	Conversion of C_{60}	Main Product (yield)
1	C_6H_5Cl	C_6H_5Cl	100%	$C_{60}(C_6H_4Cl)_5Cl$ (25%)
2	C_6H_5Cl	CH_2Cl_2	87%	$C_{60}(C_6H_4Cl)_5Cl$ (10%)
3	C_6H_5Cl	$CHCl_3$	89%	$C_{60}(C_6H_4Cl)_5Cl$ (12%)
4	C_6H_5Cl	1,1,2,2-Tetrachloroethane	95%	$C_{60}(C_6H_4Cl)_5Cl$ (29%)
5	C_6H_5Br	1,1,2,2-Tetrachloroethane	95%	$C_{60}(C_6H_4Br)_5Cl$ (23%)
6	C_6H_5I	1,1,2,2-Tetrachloroethane	97%	$C_{60}(C_6H_4I)_5Cl$ (18%)
7	C_6H_5F	1,1,2,2-Tetrachloroethane	97%	$C_{60}(C_6H_4F)_5Cl$ (12%)



Scheme 2 Functionalization of C_{60} with $FeCl_3$ and halogenated benzene in 1,1,2,2,-tetrachloroethane.

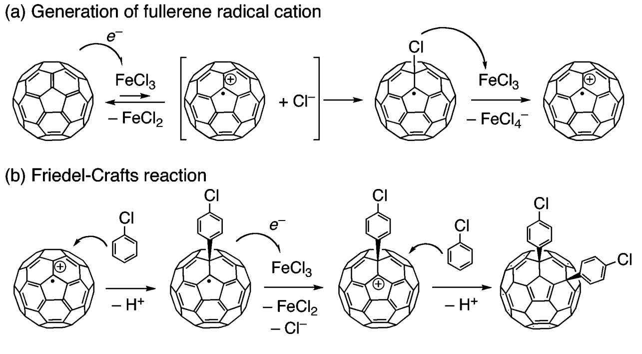
that takes part in the Friedel–Crafts reaction. The advantage of this method is that the amount of substrate can be controlled. In fact, decreasing the substrate, this reaction system gave better yield (29%) of the penta-adduct product and less of the multi (hepta, octa, and deca)-adduct products. Brominated, iodinated, and fluorinated benzenes also successfully reacted in 1,1,2,2-tetrachloroethane to give excellent C_{60} conversion (Table 1, entries 5–7). Products **2–4** (Scheme 2) contain the chlorine atoms on the cyclopentadienyl moiety of the C_{60} core; it is likely that this chlorine atom comes from $FeCl_3$. These chlorinated fullerene derivatives have already been reported,[13] and are known to have unique electrochemical properties.[14] However, the synthesis required many steps and started from $C_{60}Cl_6$.[15,16] or penta(organo)[60]fullerenes.[17] The present method involves a one-step synthesis without a complex procedure.

Finally, we propose two reaction mechanisms of this reaction. One is a hydroarylation–oxidation mechanism, while the other is an electron transfer mechanism. As for the former mechanism (Scheme 3), at first, similar to the $AlCl_3$-mediated Friedel–Crafts reaction of C_{60},[10,18] hydroarylation of C_{60} occurs in the presence of $FeCl_3$ to produce an arylhydrofullerene, $C_{60}ArH$. This hydroarylated product is oxidized by $FeCl_3$ to afford a arylfullerene cation,[19,20] $C_{60}Ar^+$, which undergoes second Friedel–Crafts reaction to give a diarylfullerene, $C_{60}Ar_2$.[21] The same reaction proceeds on $C_{60}Ar_2$ to give pentaarylated fullerene cation, $C_{60}Ar_5{}^+$, which is chlorinated to yield $C_{60}Ar_5Cl$. Further reactions can occur at the pentaarylchloro[60]fullerene to give polyarylated products bearing more than five aryl groups.



Scheme 3 Proposed reaction mechanism: hydroarylation and oxidation mechanism.

The latter proposed mechanism is rather daring (Scheme 4) from the view point of oxidation potentials of C_{60} and $FeCl_3$.[22] Single electron transfer occurs from C_{60} to $FeCl_3$ to generate fullerene radical cation. This step is actually chlorination of fullerene to afford $ClC_{60}{}^\bullet$, but the generated chlorinated compound can undergoes de-chlorination by $FeCl_3$ affording fullerene radical cation. This active species can take part in the Friedel–Crafts reaction to afford arylfullerene radical, $ArC_{60}{}^\bullet$. Oxidation of this radical species by $FeCl_3$ generates the cation to proceed the Friedel–Crafts reaction.



Scheme 4 Proposed reaction mechanism: electron transfer mechanism.

On both reaction mechanisms, we think oxidation ability of $FeCl_3$ plays an important role to proceed this reaction. In addition, halogenated aryl groups as well as chlorinated solvents seem to stabilize a key intermediate, arylfullerene cation $C_{60}Ar^+$, which has been shown by Kitagawa, *et al.*[19]

Conclusion

We have described a new $FeCl_3$-mediated polyarylation of C_{60}, which produces in quantitative conversion a polyarylated fullerene mixture containing pentaaryl(chloro)[60]fullerenes in up to 29% yield and polyarylated product having more than five aryl groups. This simple, low-cost method could be applied to industrial-scale production. The successful use of $FeCl_3$ in this method is of particular interest from the viewpoint of a ubiquitous element strategy that avoids the use of rare metals and expensive noble metals.

Experimental section

General

All reactions were carried out under argon or nitrogen atmosphere. Analytical gradient reversed-phase HPLC was performed on an Agilent 1200 series instrument equipped with an ODS column (YMC-Pack ODS-AM, 5 micron, 4.6 × 150 mm). All runs used linear gradients of methanol (solvent A) and toluene (solvent B). The gradient ran from 25% B up to 55% B over 25 min. Flow rate was 1.0 mL min^{-1} and routine UV detection was performed at 290 nm. All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 400 NMR spectrometer system. NMR spectra are reported in part per million from internal tetramethylsilane (δ 0.00 ppm) for ^1H NMR and from $CDCl_3$ (δ 77.00 ppm) for

^{13}C NMR. Mass spectra were measured with Agilent1100LC/MS (APPI, Negative mode) equipped on an ODS column (YMC-Pack ODS-AM). Preparative HPLC was performed on a Buckyprep column (Nacalai Tesque Inc., 20 mm × 250 mm) using toluene/methanol (7/3) as eluent (flow rate: 10 mL min^{-1}, detected at 290 nm with an UV spectrometer, Shimadzu SPD-6AV).

Materials

Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Sigma–Aldrich Co., Wako Pure Chemical Industries, or other commercial suppliers and used after appropriate purification. [60]Fullerene (99.5%) was purchased from Frontier Carbon Corporation. Iron(III)chloride was purchased from Wako Pure Chemical Industries and used as received.

Synthesis of 1

To a mixture of C_{60} (501 mg, 0.70 mmol) and iron(III) chloride (1.13 g, 6.97 mmol) was added chlorobenzene (25 mL) at room temperature. After stirred for 2 h, the reaction mixture was quenched with water (0.5 mL). The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude product contained the desired penta-adduct **1** mainly, and small amounts of polyarylated products as analyzed by HPLC (YMC-Pack ODS-AM) as shown in Figure S1.† Purification with HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID × 250 mm, monitored at 308 nm, eluent: toluene/methanol = 7/3) gave the title compound $C_{60}(C_6H_4\text{-Cl-4})_5Cl$ as orange powder (228 mg, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02–7.08 (m, 4H, C_6H_4), 7.23 (d, J = 8.8 Hz, 4H, C_6H_4), 7.30 (d, J = 8.8 Hz, 4H, C_6H_4), 7.40–7.49 (m, 4H, C_6H_4), 7.61–7.80 (m, 4H, C_6H_4); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 57.28 (2C, sp^3-C_{60}), 59.96 (2C, sp^3-C_{60}), 62.65 (1C, sp^3-C_{60}), 75.85(1C, C(sp^3-C_{60})-Cl), 128.06 (1C, C_6H_4Cl), 128.94 (4C, C_6H_4Cl), 129.00 (4C, C_6H_4Cl), 129.36 (4C, C_6H_4Cl), 129.49 (4C, C_6H_4Cl), 130.85 (2C, C_6H_4Cl), 133.90 (2C, C_6H_4Cl), 134.33 (2C, C_6H_4Cl), 134.36 (2C, C_6H_4Cl), 134.99 (2C, C_6H_4Cl), 136.50 (2C, C_6H_4Cl), 141.13 (2C), 142.58 (2C), 142.62 (2C), 142.86 (1C, C_6H_4Cl), 143.01 (2C), 143.34 (2C), 143.36 (2C), 144.12 (2C), 144.18 (2C), 144.28 (2C), 144.44 (2C), 144.56 (2C), 144.71 (2C), 145.75 (2C), 146.95 (2C+1C), 147.09 (2C), 148.00 (1C), 148.07 (2C), 148.43 (2C), 148.53 (2C), 148.54 (6C), 148.57 (2C), 149.41 (2C), 150.26 (2C), 153.19 (2C), 155.81 (2C); APPI-MS (–): calcd for $C_{90}H_{20}Cl_5$ [M-Cl]-), 1278.4; found, 1279.0; Anal. Calcd for $C_{90}H_{20}Cl_6$, C 82.28; H, 1.53. Found: C 81.90; H, 1.66.

Alternative synthetic method using solvent

To a mixture of C_{60} (500 mg, 0.70 mmol) and iron(III) chloride (1.13 g, 6.97 mmol) was added 1,1,2,2-tetrachloroethane (25 mL) followed by chlorobenzene (470 mg, 4.18 mmol) at room temperature. After stirred for 4 h, the reaction mixture was quenched with water (0.5 mL). The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude product contained the desired-penta adduct **1** mainly, and small amounts of polyarylated products as well as a trace amount of unreacted C_{60} as analyzed by HPLC (YMC-Pack ODS-AM) as shown in Figure S2.† Purification with HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID × 250 mm, monitored at 308 nm, eluent: toluene/methanol = 7/3) gave compound **1** as orange powder (265 mg, 29%).

Synthesis of 2

To a mixture of C_{60} (500 mg, 0.70 mmol) and iron(III) chloride (1.13 g, 6.97 mmol) was added 1,1,2,2-tetrachloroethane (25 mL) followed by bromobenzene (650 mg, 4.14 mmol) at room temperature. After stirred for 6 h, the reaction mixture was quenched with water (0.5 mL). The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude product contained the desired penta adduct **2** mainly, and small amounts of polyarylated products as well as a trace amount of unreacted C_{60} as analyzed by HPLC (YMC-Pack ODS-AM) as shown in Figure S3.† Purification with HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID × 250 mm, monitored at 308 nm, eluent: toluene/methanol = 7/3) gave compound **2** as orange powder (245 mg, 23%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (d, J = 8.8 Hz, 2H, C_6H_4), 7.22 (d, J = 8.8 Hz, 2H, C_6H_4), 7.39 (s, 8H, C_6H_4), 7.44 (d, J = 8.4 Hz, 4H, C_6H_4), 7.70 (d, J = 8.4 Hz, 4H, C_6H_4); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 57.53 (2C, sp^3-C_{60}), 60.18 (2C, sp^3-C_{60}), 62.88 (1C, sp^3-C_{60}), 75.78 (1C, C(sp^3-C_{60})-Cl), 129.83 (4C, C_6H_4Br), 129.92 (4C, C_6H_4Br), 130.74 (2C, C_6H_4Br), 131.19 (2C, C_6H_4Br), 131.29 (2C, C_6H_4Br), 132.04 (4C, C_6H_4Br), 132.10 (4C, C_6H_4Br), 134.14 (4C, C_6H_4Br), 135.54 (2C, C_6H_4Br), 137.32 (2C, C_6H_4Br), 142.65 (2C), 142.75 (2C), 142.93 (2C), 143.45 (2C), 143.48 (2C), 144.20 (2C), 144.26 (2C), 144.40 (2C), 144.52 (2C), 144.73 (2C), 144.84 (2C), 145.86 (2C), 147.10 (2C+1C), 147.23 (2C), 148.14 (1C), 148.33 (2C), 148.39 (2C), 148.57 (2C), 148.67 (6C), 148.71 (2C), 149.23 (2C), 150.40 (2C), 153.07 (2C), 155.90 (2C); APPI-MS (–): calcd for $C_{90}H_{20}Br_5$ [M-Cl]-), 1500.6; found, 1500.6; Anal. Calcd for $C_{90}H_{20}Br_5Cl$, C 70.37; H, 1.31. Found: C 70.36; H, 1.36.

Synthesis of 3

To a mixture of C_{60} (501 mg, 0.70 mmol) and iron(III) chloride (1.13 g, 6.97 mmol) was added 1,1,2,2-tetrachloroethane (25 mL) followed by iodobenzene (850 mg, 4.17 mmol) at room temperature. After stirred for 4 h, the reaction mixture was quenched with water (0.5 mL). The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude product contained the desired penta adduct **3** mainly, and small amounts of polyarylated products as well as a trace amount of unreacted C_{60} as analyzed by HPLC (YMC-Pack ODS-AM) as shown in Figure S4.† Purification with HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID × 250 mm, monitored at 308 nm, eluent: toluene/methanol = 7/3) gave compound **3** as orange powder (221 mg, 18%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (d, J = 8.8 Hz, 2H, C_6H_4), 7.26 (d, J = 8.8 Hz, 4H, C_6H_4), 7.42 (d, J = 8.8 Hz, 4H, C_6H_4), 7.54–7.60 (m, 8H, C_6H_4), 7.64 (d, J = 8.8 Hz, 4H, C_6H_4); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 57.63 (2C, sp^3-C_{60}), 60.27 (2C, sp^3-C_{60}), 62.99 (1C, sp^3-C_{60}), 75.67(1C, C(sp^3-C_{60})-Cl), 130.01 (4C, C_6H_4I), 130.10 (4C, C_6H_4I), 131.52 (2C, C_6H_4I), 136.56 (2C, C_6H_4I), 137.11 (2C, C_6H_4I), 137.98 (4C, C_6H_4I), 138.04 (4C, C_6H_4I), 142.62 (2C), 142.67 (2C), 142.74 (2C), 142.92 (8C, C_6H_4I), 143.14 (2C), 143.42 (2C), 144.17 (2C), 144.25 (2C), 144.37 (2C), 144.51 (2C), 144.72 (2C), 144.83 (2C), 145.82 (2C), 147.10 (2C+1C), 147.23 (2C), 147.73 (1C), 148.20 (2C), 148.38 (2C), 148.55 (2C), 148.66 (6C), 148.70 (2C), 149.44 (2C), 150.37 (2C), 153.39 (2C), 155.85 (2C); APPI-MS (–): calcd for $C_{90}H_{20}I_5$ [M-Cl]-), 1735.6; found, 1734.6; Anal. Calcd for $C_{90}H_{20}I_5Cl$, C 61.03; H, 1.14. Found: C 61.02; H, 0.65.

Synthesis of 4

To a mixture of C_{60} (502 mg, 0.70 mmol) and iron(III) chloride (1.14 g, 7.03 mmol) was added 1,1,2,2-tetrachloroethane (25 mL) followed by fluorobenzene (402 mg, 4.18 mmol) at room temperature. After stirred for 4 h, the reaction mixture was quenched with water (0.5 mL). The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude product contained the desired penta adduct **4** mainly, and small amounts of polyarylated products as well as a trace amount of unreacted C_{60} as analyzed by HPLC (YMC-Pack ODS-AM) as shown in Figure S4.† Purification with HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID × 250 mm, monitored at 308 nm, eluent: toluene/methanol = 7/3) gave compound **4** as orange powder (103 mg, 12%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.80–6.85 (m, 2H, C_6H_4), 6.99–7.09 (m, 8H, C_6H_4), 7.13–7.17 (m, 2H, C_6H_4), 7.56–7.59 (m, 4H, C_6H_4), 7.87–7.90 (m, 4H, C_6H_4); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 57.39 (2C, sp^3-C_{60}), 60.06 (2C, sp^3-C_{60}), 62.78 (1C, sp^3-C_{60}), 77.17(1C, C(sp^3-C_{60})-Cl), 115.04 (2C, C_6H_4F), 115.72 (4C, C_6H_4F), 115.95 (4C, C_6H_4F), 129.93 (4C, C_6H_4F), 130.05 (4C, C_6H_4F), 130.09 (4C, C_6H_4F), 131.40 (2C, C_6H_4F), 131.48 (2C, C_6H_4F), 132.64 (2C, C_6H_4F), 134.22 (2C, C_6H_4F), 142.91 (4C), 143.28 (2C), 143.62 (2C), 143.70 (2C), 144.20 (2C), 144.26 (2C), 144.41 (2C), 144.51 (2C), 144.82 (2C), 144.95 (2C), 146.16 (2C), 147.15 (2C), 147.28 (2C+1C), 147.76 (2C), 148.15 (1C), 148.23 (2C), 148.40 (2C), 148.61 (2C), 148.69 (6C), 148.72 (2C), 149.87 (2C), 150.68 (2C), 153.42 (2C), 156.28 (2C); APPI-MS (–): calcd for $C_{90}H_{20}F_5$ [M-Cl]-), 1196.1; found, 1196.1; Anal. Calcd for $C_{90}H_{20}F_5Cl$, C 87.77; H, 1.64. Found: C 88.07; H, 1.17.

Notes and references

1 (*a*) J. B. Howard, J. T. McKinnon, Y. Makarovsky, A. L. Lafleur and M. E. Johnson, *Nature*, 1991, **352**, 139–141; (*b*) J. B. Howard, J. T. McKinnon, M. E. Johnson, Y. Makarovsky and A. L. Lafleur, *J. Phys. Chem.*, 1992, **96**, 6657–6662; (*c*) H. Takehara, M. Fujiwara, M. Arikawa, M. D. Diener and J. M. Alford, *Carbon*, 2005, **43**, 311–319.

2 (*a*) J. L. Atwood, G. A. Koutsantonis and C. L. Raston, *Nature*, 1994, **368**, 229; (*b*) T. Suzuki, K. Nakashima and S. Shinkai, *Chem. Lett.*, 1994, 699–702; (*c*) K. Nagata, E. Dejima, Y. Kikuchi and M. Hashiguchi, *Chem. Lett.*, 2005, **34**, 178–179; (*d*) K. Nagata, E. Dejima, Y. Kikuchi and M. Hashiguchi, *Org. Process Res. Dev.*, 2005, **9**, 660–662.

3 (*a*) J. Li, A. Takeuchi, M. Ozawa, X. Li, K. Saigo and K. Kitazawa, *J. Chem. Soc., Chem. Commun.*, 1993, 1784–1995; (*b*) L. Y. Chiang, L. Y. Wang, J. W. Swirczewski, S. Soled and S. Cameron, *J. Org. Chem.*, 1994, **59**, 3960–3968; (*c*) K. Kokubo, K. Matsubayashi, H. Tategaki, H. Takada and T. Oshima, *ACS Nano*, 2008, **2**, 327–333; (*d*) G. Zhang, Y. Liu, D. Liang, L. Gan and Y. Li, *Angew. Chem., Int. Ed.*, 2010, **49**, 5293–5295; (*e*) G. W. Wang, Y. Murata, K. Komatsu and T. S. M. Wan, *Chem. Commun.*, 1996, 2059–2060.

4 H. Oizumi, K. Tanaka, K. Kawakami and T. Itani, *Jpn. J. Appl. Phys.*, 2011, **49**, 06GF04.

5 (*a*) K. Hinokuma and M. Ata, *Chem. Phys. Lett.*, 2001, **341**, 442–446; (*b*) R. Maruyama, *Electrochim. Acta*, 2002, **48**, 85–89; (*c*) T. Hirakimoto, K. Fukushima, Y Li, S. Takizawa, K. Hinokuma and T. Senoo, *214th Meeting of Electrochemical Society*, 2008, 1108; (*d*) M. E. Lyn, J. He and B. Koplitz, *Appl. Surf. Sci.*, 2005, **246**, 44–47.

6 H. Peng, F. S. M. Leung, A. X. Wu, Y. Dong, Y. Dong, N.-T. Yu, X. Feng and B. Z. Tang, *Chem. Mater.*, 2004, **16**, 4790–4798.

7 M. Lenes, G.-J. A. H. Wetzelaer, F. B. Kooistra, S. C. Veenstra, J. C. Hummelen and P. W. M. Blom, *Adv. Mater.*, 2008, **20**, 2116–2119.

8 (*a*) S. Zhou, C. Burger, B. Chu, M. Sawamura, N. Nagahama, M. Toganoh, U. E. Hackler, H. Isobe and E. Nakamura, *Science*, 2001, **291**, 1944–1947; (*b*) H. Isobe, T. Homma and E. Nakamura, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 14895–14898; (*c*) M. Sawamura, K. Kawai, Y. Matsuo, K. Kanie, T. Kato and E. Nakamura, *Nature*, 2002, **419**, 702–705; (*d*) Y. Matsuo, A. Muramatsu, Y. Kamikawa, T. Kato and E. Nakamura, *J. Am. Chem. Soc.*, 2006, **128**, 9586–9587; (*e*) Y.-W. Zhong, Y. Matsuo and E. Nakamura, *J. Am. Chem. Soc.*, 2007, **129**, 3052–3053; (*f*) Y. Matsuo, K. Morita and E. Nakamura, *Chem.–Asian J.*, 2008, **3**, 1350–1357; (*g*) Y. Matsuo, K. Kanaizuka, K. Matsuo, Y.-W. Zhong, T. Nakae and E. Nakamura, *J. Am. Chem. Soc.*, 2008, **130**, 5016–5017.

9 (*a*) A. Hirsch, M. Brettreich, *Fullerenes, Chemistry and Reactions*, Wiley-VCH, Weinheim, 2005; (*b*) Y. Murata, K. Komatsu and T. S. M. Wan, *Tetrahedron Lett.*, 1996, **37**, 7061–7064; (*c*) A. Hirsch, T. Grosser, A. Skiebe and A. Soi, *Chem. Ber.*, 1993, **126**, 1061–1067; (*d*) A. Hirsch, *Synthesis*, 1995, 895–913; (*e*) M. Sawamura, H. Iikura and E. Nakamura, *J. Am. Chem. Soc.*, 1996, **118**, 12850–12851; (*f*) Y. Matsuo, K. Tahara, K. Morita, K. Matsuo and E. Nakamura, *Angew. Chem., Int. Ed.*, 2007, **46**, 2844–2847; (*g*) M. Nambo, R. Noyori and K. Itami, *J. Am. Chem. Soc.*, 2007, **129**, 8080–8081.

10 (*a*) G. A. Olah, I. Bucsi, C. Lambert, R. Aniszfeld, N. J. Trivedi, D. K. Sensharma and G. K. S. Prakash, *J. Am. Chem. Soc.*, 1991, **113**, 9387–9388; (*b*) A. Iwashita, Y. Matsuo and E. Nakamura, *Angew. Chem., Int. Ed.*, 2007, **46**, 3513–3517.

11 S. H. Hoke, J. Molstad, G. L. Payne, R. Kahr, D. Ben-Amotz and R. G. Cooks, *Rapid Commun. Mass Spectrom.*, 1991, **5**, 472–474.

12 (*a*) Y. Matsuo, K. Tahara, M. Sawamura and E. Nakamura, *J. Am. Chem. Soc.*, 2004, **126**, 8725–8734; (*b*) Y. Matsuo and E. Nakamura, *J. Am. Chem. Soc.*, 2005, **127**, 8457–8466.

13 (*a*) A. G. Avent, P. R. Birkett, J. D. Crane, A. D. Darwish, G. J. Langley, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1994, 1463–1464; (*b*) P. R. Birkett, A. G. Avent, A. D. Darwish, I. Hahn, H. W. Kroto, G. J. Langley, J. O'Loughlin, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1121–1126.

14 P. R. Birkett, R. Taylor, N. K. Wachter, M. Carano, F. Paolucci, S. Roffia and F. Zerbetto, *J. Am. Chem. Soc.*, 2000, **122**, 4209–4212.

15 P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1993, 1230–1232.

16 (*a*) G. A. Olah, I. Bucsi, C. Lambert, R. Aniszfeld, N. J. Trivedi, D. K. Sensharma and G. K. S. Prakash, *J. Am. Chem. Soc.*, 1991, **113**, 9385–9387; (*b*) R. Taylor, G. J. Langley, M. F. Meidine, J. P. Parsons, A. K. Abdul-Sada, T. J. Dennis, J. P. Hare, H. W. Kroto and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 667–668.

17 Y. Matsuo, Y. Kuninobu, A. Muramatsu, M. Sawamura and E. Nakamura, *Organometallics*, 2008, **27**, 3403–3409.

18 It has been known that small amount of water generates an activated proton to proceed the $AlCl_3$-mediated Friedel–Crafts reaction. See ref. 10.

19 (*a*) T. Kitagawa, H. Sakamoto and K. Takeuchi, *J. Am. Chem. Soc.*, 1999, **121**, 4298–4299; (*b*) T. Kitagawa and K. Takeuchi, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 785–800; (*c*) T. Kitagawa, Y. Lee, M. Hanamura, H. Sakamoto, H. Konno, K. Takeuchi and K. Komatsu, *Chem. Commun.*, 2002, 3062–3063.

20 Y. Zhang, Y. Matsuo, C.-Z. Li, H. Tanaka and E. Nakamura, *J. Am. Chem. Soc.*, 2011, **133**, 8086–8089.

21 Y. Matsuo, Y. Zhang, I. Soga, Y. Sato and E. Nakamura, *Tetrahedron Lett.*, 2011, **52**, 2240–2242.

22 Oxidation potential for C_{60}: +1.26V *vs.* Fc/Fc^+. Reduction potential for $FeCl_3$: 0.77V *vs.* NHE (= 0.1~0.2V *vs.* Fc/Fc^+). We think coordination of C_{60} to $FeCl_3$ may change oxidation and reduction potentials.