

# Synthesis of two pentaarylated [60] fullerene derivatives $\text{Ar}_5\text{C}_{60}\text{H}$ ( $\text{Ar} = p\text{-MeC}_6\text{H}_4, m\text{-MeC}_6\text{H}_4$ ) and their novel electrochemical properties

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Through one pot reaction of  $\text{C}_{60}$  with organocopper/magnesium reagent ( $p\text{-MeC}_6\text{H}_4$ )<sub>2</sub> CuMgBr or ( $m\text{-MeC}_6\text{H}_4$ )<sub>2</sub> CuMgBr prepared from CuBr·Me<sub>2</sub>S and  $p\text{-MeC}_6\text{H}_4\text{MgBr}$  or  $m\text{-MeC}_6\text{H}_4\text{MgBr}$  and subsequent quenching with aqueous  $\text{NH}_4\text{Cl}$ , two pentaarylated [60] fullerene derivatives ( $p\text{-MeC}_6\text{H}_4$ )<sub>5</sub> $\text{C}_{60}\text{H}$  (1) and ( $m\text{-MeC}_6\text{H}_4$ )<sub>5</sub> $\text{C}_{60}\text{H}$  (2) have been synthesized in 94% and 96% yields, respectively. While known compound 1 prepared via this improved method is unambiguously identified, new compound 2 is fully characterized by elemental analysis, IR, UV-vis, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopies. Additionally, electrochemical study shows that the two [60] fullerene derivatives 1 and 2 in dichloromethane solution display two sequential one-electron reductions which are shifted by about 0.4 V towards more negative potential values with respect to free  $\text{C}_{60}$ . Such remarkable cathodic shift is attributed to the multiple breakage of the double-bond conjugation within the fullerene core.

**Keywords** [60] Fullerene, pentaarylated derivatives, synthesis, electrochemical properties

## Introduction

The pentaarylated [60] fullerene derivatives with a general formula  $\text{Ar}_5\text{C}_{60}\text{H}$  ( $\text{Ar} =$  aromatic groups) have currently attracted great attention, because of their unique structures, novel properties and important uses in preparation of an entirely new class of cyclopentadienyl metal complexes.<sup>1-4</sup> For preparation of  $\text{Ar}_5\text{C}_{60}\text{H}$ , two

synthetic routes starting from  $\text{C}_{60}$ , have been so far reported. One is multistep synthesis<sup>1,2</sup> and the other is one pot synthesis.<sup>3</sup> For example, pentaphenyl[60] fullerene compound  $\text{Ph}_5\text{C}_{60}\text{H}$  (3) can be prepared via either three steps of chlorination of  $\text{C}_{60}$ , arylation of  $\text{C}_{60}\text{Cl}_5$  and reduction of  $\text{Ph}_5\text{C}_{60}\text{Cl}$ <sup>1,2</sup> or through one pot reaction of  $\text{C}_{60}$  with organocopper/magnesium reagent  $\text{Ph}_2\text{CuMgBr}$  followed by quenching with aqueous  $\text{NH}_4\text{Cl}$ .<sup>3</sup> Apparently, except high yields the one pot synthesis is more convenient and less costly than the multistep synthesis in preparation of [60] fullerene derivatives. However, up to now among the derivatives of type  $\text{Ar}_5\text{C}_{60}\text{H}$ , only  $\text{Ph}_5\text{C}_{60}\text{H}$  has been reported to be prepared by one pot synthesis. This paper will describe the applicability of the one pot synthesis for preparation of other  $\text{Ar}_5\text{C}_{60}\text{H}$  derivatives, such as ( $p\text{-MeC}_6\text{H}_4$ )<sub>5</sub> $\text{C}_{60}\text{H}$  (1) and ( $m\text{-MeC}_6\text{H}_4$ )<sub>5</sub> $\text{C}_{60}\text{H}$  (2), as well as a comparative study of the electrochemical properties of 1, 2 and  $\text{C}_{60}$  itself.

## Results and discussion

### Synthesis and characterization of 1 and 2

It was found that the one pot reaction of  $\text{C}_{60}$  with an excess amount of organocopper/magnesium reagent prepared from an equimolar  $p\text{-MeC}_6\text{H}_4\text{MgBr}$  or  $m\text{-MeC}_6\text{H}_4\text{MgBr}$  and CuBr·SMe<sub>2</sub> in a mixed solvent from

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$-78^{\circ}\text{C}$  to rt, followed by quenching with aqueous  $\text{NH}_4\text{Cl}$  afforded two corresponding pentaarylated [60]-fullerene derivatives ( $p\text{-MeC}_6\text{H}_4$ ) $_5\text{C}_{60}\text{H}$  (**1**) in 94% yield and ( $m\text{-MeC}_6\text{H}_4$ ) $_5\text{C}_{60}\text{H}$  (**2**) in 96% yield, respectively. It is worth noting that although derivative **1** was previously prepared by a multistep procedure,<sup>1,2</sup> the yield is much lower (51% on the basis of  $\text{C}_{60}$ ) than that (94%) obtained by this one pot synthesis. In addition, the attempted preparations of ( $o\text{-MeC}_6\text{H}_4$ ) $_5\text{C}_{60}\text{H}$  and ( $o, p, o\text{-Me}_3\text{C}_6\text{H}_2$ ) $_5\text{C}_{60}\text{H}$  via one pot synthesis have proved to be unsuccessful, possibly due to the steric hindrance arising from the  $o$ -methyl groups in corresponding organocopper/magnesium reagents. **1** and **2** are orange

or orange-red, air-stable crystals, which do not melt even heated up to  $350^{\circ}\text{C}$  in nitrogen. **1** is less soluble than **2** in common organic solvents, such as toluene, THF and dichloromethane and the solubility of **1** in toluene increases remarkably as the temperature rises.

The structure of known derivative **1** (Fig. 1) was identified by comparison of its combustion analysis, IR, UV-vis and  $^1\text{H}$  NMR spectra with corresponding those reported in the previous literature.<sup>2</sup> The structure of new derivative **2** (Fig. 1) was characterized by elemental analysis, IR, UV-vis,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopies.

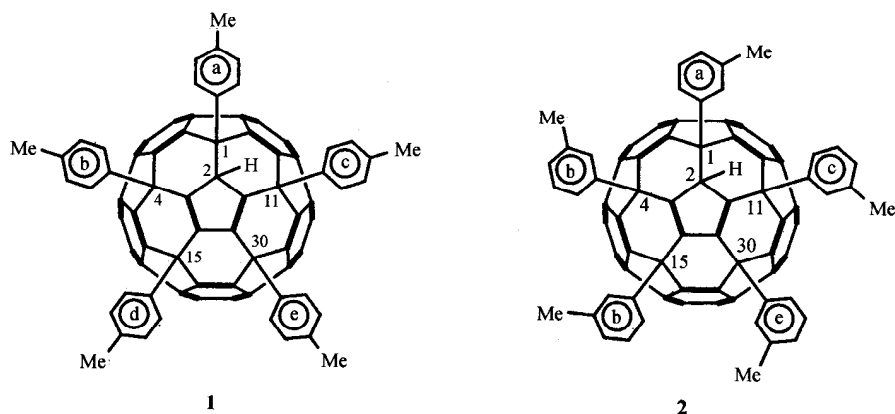


Fig. 1 Structures of **1** and **2**.

The IR spectrum of **2**, similar to that of **1**,<sup>2</sup> shows both aromatic and aliphatic C—H stretching vibrations for its  $m$ -tolyl groups at 3021, 2948, 2916 and 2857  $\text{cm}^{-1}$ , whereas it displays its aromatic C—C stretching vibrations for its  $m$ -tolyl groups at 1605, 1587, 1485 and 1459  $\text{cm}^{-1}$ . In addition, the IR spectrum of **2** exhibits four absorption bands at 1418, 1172, 587 and 544  $\text{cm}^{-1}$ , characteristic of the C—C stretching vibrations of its  $\text{C}_{60}$  cage.<sup>5,6</sup> The UV-vis spectra of **1**, **2** and free  $\text{C}_{60}$  are shown in Fig. 2. As seen from Fig. 2, the spectrum of **2** is almost identical with that of **1**, except 1–5 nm shift for their absorption bands. In addition, while the first band at 230 nm for free  $\text{C}_{60}$  is much weaker than its second band at 257 nm, the first band at 236 nm for **1** and at 231 nm for **2** are stronger than their second bands at 259 nm for **1** and at 258 nm for **2**. This is most likely due to some overlap of those two bands at around 230 nm generated from the  $\text{C}_{60}$  cage and the aromatic tolyl groups in derivatives **1** and **2**.<sup>6,7</sup> The  $^1\text{H}$

NMR spectrum of **2** shows one multiplet in the range of  $\delta$  7.08–7.50, which can be assigned to twenty protons on the five benzene rings a–e. Since the multiplet is much more complicated than corresponding that displayed by **1**,<sup>2</sup> it cannot be clearly assigned to specific protons on these benzene rings. In addition, the  $^1\text{H}$  NMR spectrum of **2** displays one singlet at  $\delta$  2.02, one singlet at  $\delta$  2.06, one singlet at  $\delta$  2.18 and one singlet at  $\delta$  5.27. Similar to the assignments in **1**, these singlets might be assigned to one  $m\text{-Me}$  group in ring a, two  $m\text{-Me}$  groups in rings d, e, two  $m\text{-Me}$  groups in rings b, c and the hydrogen bonded to C-2 respectively. It is noteworthy that the chemical shifts of  $m\text{-Me}$  groups in **2** lie in higher field than those of  $p\text{-Me}$  groups in **1**.<sup>2</sup> This is probably because that the  $\text{C}_{60}$  core is electron-withdrawing group and thus the  $p\text{-Me}$  groups are more deshielded than  $m\text{-Me}$  groups. Furthermore, the chemical shift of the hydrogen bonded to C-2 in parent compound  $\text{Ph}_5\text{C}_{60}\text{H}$  (**3**) ( $\delta$  5.31)<sup>2,3</sup> is greater than that in

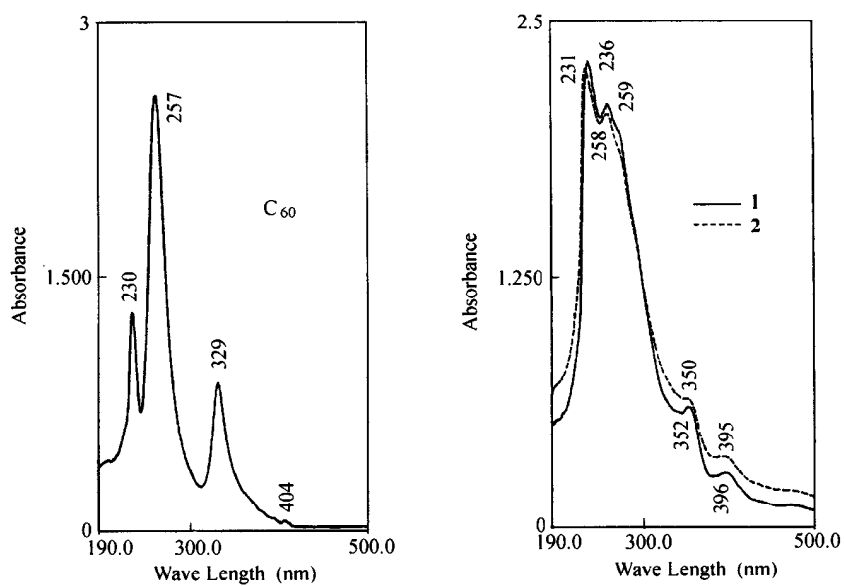


Fig. 2 UV-vis spectra of 1, 2 and  $C_{60}$  in dichloromethane at room temperature.

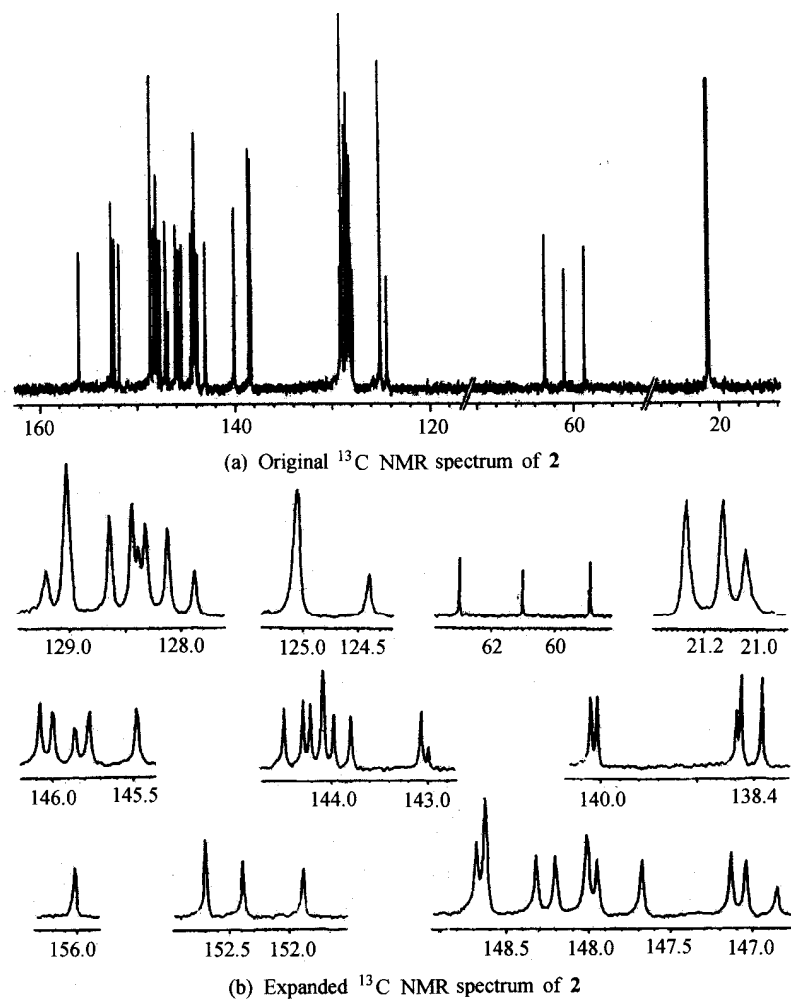


Fig. 3 Original  $^{13}C$  NMR spectrum of 2 and its expanded  $^{13}C$  NMR spectrum.

(*m*-MeC<sub>6</sub>H<sub>4</sub>)<sub>5</sub>C<sub>60</sub>H (**2**) and in turn greater than that in (*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>5</sub>C<sub>60</sub>H (**1**).<sup>3</sup> This is apparently that both *p*-Me and *m*-Me are electron-releasing groups and the *p*-Me groups in **1** render C<sub>60</sub> core more electronegative than *m*-Me groups in **2**.

The original <sup>13</sup>C NMR spectrum of **2** and its expanded one, namely (a) and (b), are shown in Fig. 3. While from spectrum (a) some <sup>13</sup>C NMR signals, particularly those of signals for C<sub>60</sub> core, cannot be obviously seen, spectrum (b) shows each of the <sup>13</sup>C NMR signals of **2** clearly. In sp<sup>3</sup> region there are three peaks at δ 21.04, 21.13 and 21.26 in a 1:2:2 intensity ratio assigned to three types of *m*-Me groups of five tolyl substituents, whereas another three peaks at δ 58.91, 61.01 and 63.02 in a 1:1:1 intensity ratio attributed to C-1/C-2, C-4/C-11, and C-15/C-30 of C<sub>60</sub> moiety, respectively. Although C-1 and C-2 in **2** appear to be somewhat different, they actually show one peak at δ 58.91, whereas corresponding those in its *p*-Me analog (*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>5</sub>C<sub>60</sub>H (**1**) exhibited two very close peaks at δ 58.5 and δ 58.6<sup>2</sup> and those in its parent compound Ph<sub>5</sub>C<sub>60</sub>H (**3**) displayed two very close peaks at δ 58.31 and δ 58.42,<sup>1</sup> respectively. Since **2** is C<sub>s</sub> symmetric, the C<sub>60</sub> cage should have 32 different C and the five *m*-tolyl substituents should have 21 different C, thus displaying 32 peaks and 21 peaks, respectively. Except the 3 peaks arising from *m*-Me groups of tolyl substituents and 4 peaks (two peaks from C-1 and C-2 overlapped) arising from the C<sub>60</sub> cage mentioned above, there should be 18 peaks for five benzene rings of the tolyl substituents and 28 peaks for the C<sub>60</sub> cage. In fact, in the <sup>13</sup>C NMR spectrum of **2** there are only 15 peaks for the benzene rings and 27 peaks for the remaining C<sub>60</sub> cage. This is because that in the sp<sup>2</sup> region the benzene rings show one peak at δ 125.07 and another peak at δ 129.02 respectively in double and triple intensities, whereas in the sp<sup>2</sup> region the C<sub>60</sub> core displays one peak at δ 148.63 in double intensity of the others.

#### Electrochemistry of **1** and **2**

Fig. 4 compares the cyclic voltammetric response of (*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>5</sub>C<sub>60</sub>H (**1**) with that of C<sub>60</sub> in dichloromethane at -10°C.

It is well evident that the sequential one-electron

reductions of the fullerene moiety in the *p*-tolyl derivative are shifted by about 0.4 V towards more negative potential values with respect to free C<sub>60</sub>, so that only the two first cathodic steps are clearly detected; a third, irreversible step (not shown in the figure) is present very close to the solvent discharge ( $E_p \approx -2.05$  V). Anal-

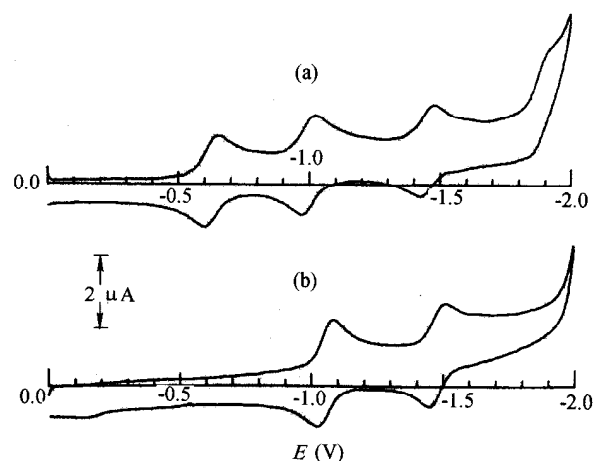


Fig. 4 Comparison of the cyclic voltammetric response recorded at a platinum electrode in CH<sub>2</sub>Cl<sub>2</sub> solutions containing [NBu<sub>4</sub>][PF<sub>6</sub>] (0.2 mol/L) and (a) C<sub>60</sub> (saturated solution); (b) (*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>5</sub>C<sub>60</sub>H (**1**) (7 × 10<sup>-4</sup> mol/L). Scan rate 0.2 V/s, T = -10°C.

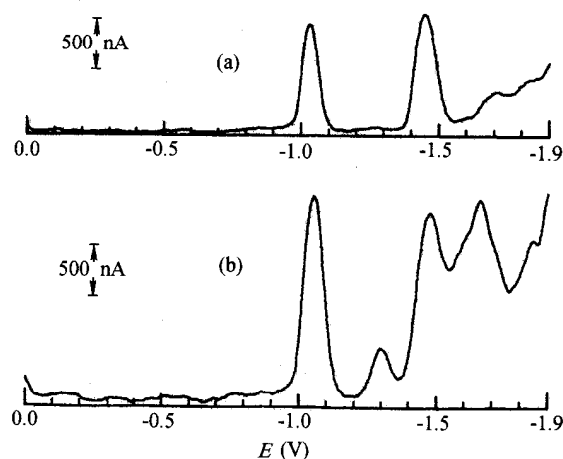


Fig. 5 Differential pulse voltammograms recorded at a platinum electrode in CH<sub>2</sub>Cl<sub>2</sub> solution containing [NBu<sub>4</sub>][PF<sub>6</sub>] (0.2 mol/L) and (*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>5</sub>C<sub>60</sub>H (**1**) (7 × 10<sup>-4</sup> mol/L). Scan rate 0.004 V/s, (a) T = -10°C; (b) +20°C.

ysis<sup>8</sup> of the cyclic voltammetric responses of the two sequential reductions with scan rate varying from 0.02 V/s to 2 V/s as well as controlled potential coulometry in correspondence of the first reduction ( $E_w = -1.2$  V) is diagnostic of chemically and electrochemically reversible, one-electron transfers. As expected, such a behaviour is quite similar to that found for its parent compound  $\text{Ph}_5\text{C}_{60}\text{H}$  (**3**), in tetrahydrofuran solution at  $-78^\circ\text{C}$ .<sup>4</sup>

As far as the electronic effects responsible for such remarkable shifts are concerned, it is well conceivable that they mainly depend upon the extended breakage of the double bond conjugation, rather than upon the inductive effects of the substituents. As a matter of fact, either the simplest  $\text{C}_{60}\text{H}_2$ <sup>9</sup> or  $\text{C}_{60}\text{HBu}-t$ <sup>10</sup> both display a cathodic shift of about 0.15 V.

In contrast to  $\text{Ph}_5\text{C}_{60}\text{H}$  (**3**), which after the first one-electron reduction at room temperature quickly deprotonates to  $\text{Ph}_5\text{C}_{60}$  free radical species,<sup>4</sup> the present pentatolylfullerene does not undergo such fast conversion in cyclic voltammetry at room temperature, even if really the second reduction becomes complicated by chemical reactions ( $i_{pa}/i_{pc} = 0.4$  at 0.2 V/s). As a matter of fact, the differential pulse voltammograms illustrated in Fig. 5 show that such a conversion partially takes place also in the present case, in that at very slow scan rates two new peaks appear at  $-1.30$  V and  $-1.65$  V, respectively.

Essentially the same behaviour is exhibited by (*m*- $\text{MeC}_6\text{H}_4$ )<sub>5</sub> $\text{C}_{60}\text{H}$  (**2**), and the electrochemical data are compiled in Table 1.

**Table 1** Formal electrode potentials (in V, vs. SCE) and peak-to-peak separations (mV) for the redox changes exhibited by the present pentatolylfullerenes and related species, in dichloromethane solution, at  $-10^\circ\text{C}$ . Values in parenthesis are referred to the  $\text{Fc}/\text{Fc}^+$  couple

Compound	$E_{0/1}'$	$\Delta E_p^a$	$E_{1-/2}'$	$\Delta E_p^a$	$E_{2-/3}'$	$\Delta E_p^a$			
$\text{C}_{60}$	-0.63	(-1.01)	59	-1.00	(-1.38)	60	-1.45	(-1.83)	64
<b>1</b>	-1.04	(-1.42)	66	-1.48	(-1.86)	64	-2.05 <sup>b</sup>	(-2.43)	—
<b>2</b>	-1.02	(-1.40)	70	-1.48	(-1.86)	78	-2.05 <sup>b</sup>	(-2.43)	—
<b>3</b>		(-1.45) <sup>c</sup>	—		(-2.10) <sup>c</sup>	—			—
$\text{C}_{60}\text{H}_2$		(-1.11) <sup>d</sup>	—		(-1.48) <sup>d</sup>	—		(-1.99) <sup>d</sup>	—
$\text{C}_{60}\text{HBu}^t$		(-1.01) <sup>e</sup>	—		(-1.57) <sup>e</sup>	—		(-2.18) <sup>e</sup>	—

<sup>a</sup> Measured at 0.2 V/s; <sup>b</sup> very close to the solvent discharge; <sup>c</sup> from Ref. 4, measured at  $-78^\circ\text{C}$ , in THF solution; <sup>d</sup> from Ref. 9, at room temperature; <sup>e</sup> from Ref. 10, measured in THF solution at room temperature.

## Experimental

All reactions were carried out under a highly-purified nitrogen atmosphere using standard Schlenk or vacuum-line techniques. Silica gel (200—300 mesh) for column chromatography (20 × 3 cm) was activated for 4 h at  $110^\circ\text{C}$ . Toluene and tetrahydrofuran were dried and deoxygenated by distillation from sodium/benzophenone ketyl. Methyl sulfide was dried over anhydrous calcium chloride and distilled. All solvents were bubbled with nitrogen for at least 15 min before use. [60] fullerene (> 99.9%) was purchased from Yin-Han Fullerene High-Tech. Co., Ltd. and used as received. Cuprous bromide methylsulfide complex  $\text{CuBr}\cdot\text{Me}_2\text{S}$  was prepared according to literature.<sup>11</sup> Arylmagnesium bromides were prepared from corresponding aryl bromides and magnesium turnings. Elemental analysis was performed using a

Yanaco CHN Corder MT-3 analyzer. The IR spectra were recorded on either a Nicolet 170SX or a Nicolet 560 E. P. S. FTIR spectrophotometer, while the UV-vis spectra were recorded on a Shimadzu UV-240 spectrometer. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were determined on a Bruker AC-P200 and a UNITY-PLUS 400 spectrometer, respectively.

### Preparation of (*p*- $\text{MeC}_6\text{H}_4$ )<sub>5</sub> $\text{C}_{60}\text{H}$ (**1**)

A 100 mL three-necked flask equipped with a magnetic stir-bar, a serum cap and a nitrogen inlet was charged with  $\text{CuBr}\cdot\text{Me}_2\text{S}$  (249 mg, 1.21 mmol) dissolved in a mixture of  $\text{Me}_2\text{S}$  (1.3 mL) and THF (1.6 mL). The solution was cooled to  $-78^\circ\text{C}$ , and then a THF solution of *p*- $\text{MeC}_6\text{H}_4\text{MgBr}$  (1.2 mmol) was dropwise added under stirring. During the period of time, the colorless solution turned to a brownish suspension of

organocopper/magnesium reagent (*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CuMgBr. To this suspension, C<sub>60</sub> (56 mg, 78 μmol) and toluene (20 mL) were added and then the mixture was stirred at -78 °C for about 0.5 h. When the mixture was allowed to warm to room temperature, it was stirred for 14 h at this temperature, and then quenched with aqueous NH<sub>4</sub>Cl and stirred violently for another 0.5 h. The organic layer was separated and dried with anhydrous CaCl<sub>2</sub>. After the solvent was removed under vacuum, the residue was chromatographed on a silica gel column using 1:1 (V:V) toluene:petroleum ether as eluent. An orange band was collected, from which (*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>5</sub>C<sub>60</sub>H (1) was obtained (85 mg, 94% based on C<sub>60</sub>). The product was further purified by recrystallization with toluene to give tiny orange crystals, mp > 350 °C. λ<sub>max</sub> (CH<sub>2</sub>Cl<sub>2</sub>): 236 (log ε 5.11), 259 (5.06), 352 (4.51), 396 (4.16) nm. ν<sub>max</sub> (KBr): 3022, 2949, 2919, 2859, 1509, 1458, 1410, 1284, 1234, 1187, 1113, 1020, 954, 905, 877, 834, 807, 757, 649, 583, 559, 537, 499, 471 cm<sup>-1</sup>. δ<sub>H</sub> (CDCl<sub>3</sub>): 2.27 (s, 3H, CH<sub>3</sub> on ring a), 2.37 (s, 6H, CH<sub>3</sub> on rings b, c), 2.31 (s, 6H, CH<sub>3</sub> on rings d, e), 5.22 (s, 1H, C<sub>60</sub>-H), 6.97—7.65 (m, 20H, C<sub>6</sub>H<sub>4</sub>). Anal. C<sub>95</sub>H<sub>36</sub>. Calcd: C, 96.98; H, 3.02. Found: C, 96.79; H, 3.35.

#### Preparation of (*m*-MeC<sub>6</sub>H<sub>4</sub>)<sub>5</sub>C<sub>60</sub>H (2)

Similar to the preparative procedure of (*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>5</sub>C<sub>60</sub>H (1) described above, the corresponding organocopper/magnesium reagent (*m*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CuMgBr prepared from CuBr·SMe<sub>2</sub> (251 mg, 1.22 mmol) and *m*-MeC<sub>6</sub>H<sub>4</sub>MgBr (1.2 mmol) was allowed to react with C<sub>60</sub> (54 mg, 75 μmol). The crude product was chromatographed on a silica gel column using 1:1 (V:V) toluene:petroleum ether as eluent. An orange-red band was collected, from which (*m*-MeC<sub>6</sub>H<sub>4</sub>)<sub>5</sub>C<sub>60</sub>H (2) (85 mg, 96% based on C<sub>60</sub>) was obtained. The product was further purified by recrystallization from dichloromethane/petroleum ether to give orange-red plates, mp > 350 °C.

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λ<sub>max</sub> (CH<sub>2</sub>Cl<sub>2</sub>): 231 (log ε 5.03), 258 (4.97), 350 (4.40), 395 (4.06) nm. ν<sub>max</sub> (KBr): 3021, 2948, 2916, 2857, 1605, 1587, 1485, 1459, 1418, 1377, 1286, 1234, 1200, 1172, 1096, 1038, 1000, 968, 879, 813, 775, 753, 697, 663, 587, 544, 490, 436, 411 cm<sup>-1</sup>. δ<sub>H</sub> (CDCl<sub>3</sub>): 2.02 (s, 3H, CH<sub>3</sub> on ring a), 2.18 (s, 6H, CH<sub>3</sub> on rings b, c), 2.06 (s, 6H, CH<sub>3</sub> on rings d, e), 5.27 (s, 1H, C<sub>60</sub>-H), 7.08—7.50 (m, 20H, C<sub>6</sub>H<sub>4</sub>). δ<sub>C</sub> (CDCl<sub>3</sub>): 21.04 (1C), 21.13 (2C), 21.26 (2C), 58.91 (2C), 61.01 (2C), 63.02 (2C), 124.40, 125.07, 127.87, 128.12, 128.32, 128.38, 128.44, 128.64, 129.02, 129.21, 138.32, 138.53, 138.59, 140.03, 140.10 (30C of five benzene rings), 142.99 (1C), 143.07 (2C), 143.80 (2C), 143.97 (2C), 144.09 (2C), 144.21 (2C), 144.29 (2C), 144.49 (2C), 145.48 (2C), 145.76 (2C), 145.86 (2C), 146.00 (2C), 146.07 (2C), 146.85 (1C), 147.04 (2C), 147.13 (2C), 147.67 (2C), 147.95 (2C), 148.01 (2C), 148.21 (2C), 148.32 (2C), 148.63 (4C), 148.68 (2C), 151.88 (2C), 152.39 (2C), 152.70 (2C), 156.02 (2C). Anal. C<sub>95</sub>H<sub>36</sub>. Calcd: C, 96.98; H, 3.02. Found: C, 96.52; H, 3.23.

#### Electrochemical determinations

Materials and apparatus for electrochemistry have been described elsewhere.<sup>12</sup> All the potential values are referred to the saturated calomel electrode (SCE). Under the present experimental conditions the one-electron oxidation of ferrocene occurs at  $E^{\circ} = +0.38$  V in the temperature range from -10 °C to +10 °C, and at  $E^{\circ} = +0.39$  V at +20 °C.

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