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$C_{60}(C_6H_4Me)_4Ph_4$: a fully substituted derivative of the pentagon-fused $C_{60}Cl_8$

Hua Liang,*[a] Ke Dai,[b] Zhi C. Guo[c] and Ru F. Peng[a]

[a] *State Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, Southwest University of Science and Technology, 621010 Mianyang, China. Fax: +86 816 241 9492; e-mail: dandelion1978@163.com*
[b] *Department of Chemistry, School of Materials Science and Engineering, Southwest University of Science and Technology, 621010 Mianyang, China*
[c] *School of National Defence Science and Technology, Southwest University of Science and Technology, 621010 Mianyang, China*

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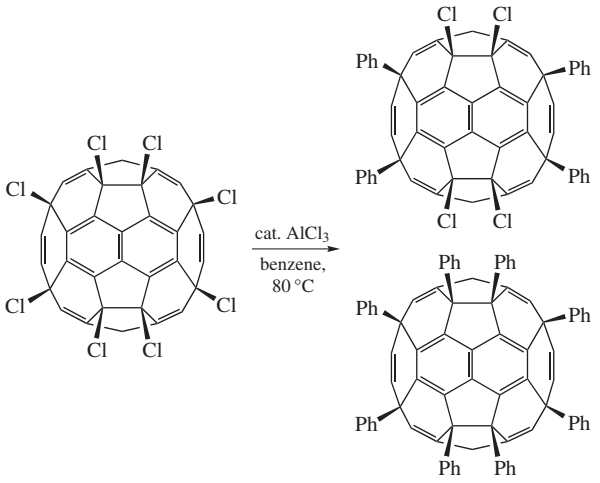
The eight chlorines of $C_{60}Cl_8$ with two pairs of fused pentagons are successfully substituted by sterically encumbering groups through the Friedel–Crafts reaction to get $C_{60}(C_6H_4Me)_4Ph_4$, which provides a facile way for multiple modification of special fullerenes.

Structurally amazing fullerenes violating the isolated pentagon rule (IPR) are a key part to understand the mechanism of fullerene formation. These fullerenes have unusual electronic properties because of a structure-caused curvature and their derivatives may have potential applications in materials science.[1–9] Only a few reports considered the derivatization of non-IPR fullerenes and most of them are related to endohedral metallofullerenes, which show relatively poor selectivity in reactions.[5,10–12] However, $C_{60}Cl_8$, the non-IPR chlorofullerene with two pairs of fused pentagons (the number nomenclature specified by Fowler's spiral algorithm[13]), shows an interesting regiospecific substitution character caused by the two kinds of chlorines, where four chlorines are connected at pentagon–pentagon (C_{pp}) fusion sites and the rest chlorines at hexagon–hexagon (C_{hh}) sites of the cage.[5] Two ways to modify $C_{60}Cl_8$ are known. According to one of them, the C_{hh}-connected chlorines can be replaced by different groups while the C_{pp}-connected chlorines kept intact through the Friedel–Crafts reaction; according to another one, both of the chlorines can be replaced by stronger nucleophiles simultaneously under alkaline conditions.[5]

Here, we modified $^{\#1809}C_{60}Cl_8$ and obtained its fully substituted derivatives, where all the chlorine atoms are replaced by sterically encumbering groups, *via* the Friedel–Crafts reactions. To achieve the substitution of all the eight chlorines, we used $AlCl_3$ as a catalyst and benzene as a reactant, which resulted in $^{\#1809}C_{60}Cl_4Ph_4$ and $^{\#1809}C_{60}Ph_8$ (Scheme 1). Hereinafter, the superscript $^{\#1809}$ in C_{60} and its derivatives will be omitted for concision.

The amount of $AlCl_3$ is crucial to the product constitution, which can be traced by MS analysis. The reaction cannot be carried out completely when the amount of $AlCl_3$ is insufficient, whereas the yield of some by-products increases when it is too excessive. The MS spectrum [Figure 1(*a*)] shows the presence of both $C_{60}Cl_4Ph_4$ (*m*/*z* 1170.2) and $C_{60}Ph_8$ (*m*/*z* 1337.3) in the product mixture when molar ratio of $C_{60}Cl_8$: $AlCl_3$ was 1:12. Lengthening the reaction time to 17 h did not result in obvious change. When the $C_{60}Cl_8$: $AlCl_3$ ratio was 1:18, $C_{60}Ph_8$ was the only product [Figure 1(*b*)]. This indicates that the generation of $C_{60}Ph_8$ in the reaction occurred in two steps: first, the four C_{hh}-connected Cl atoms were replaced by phenyl groups to get $C_{60}Cl_4Ph_4$; second, the four C_{pp}-connected Cl atoms of $C_{60}Cl_4Ph_4$ were replaced with phenyl groups to afford $C_{60}Ph_8$. The MS analysis of the product mixture at different reaction times



Scheme 1

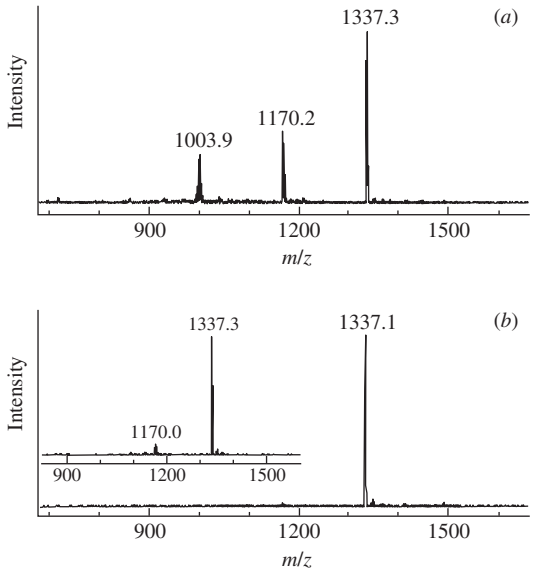


Figure 1 MS spectra of the raw product after 5 h; the $C_{60}Cl_8$: $AlCl_3$ molar ratios: (*a*) 1 : 12 and (*b*) 1 : 18 (inset: the MS spectrum of the raw material for a reaction time of 2 h).

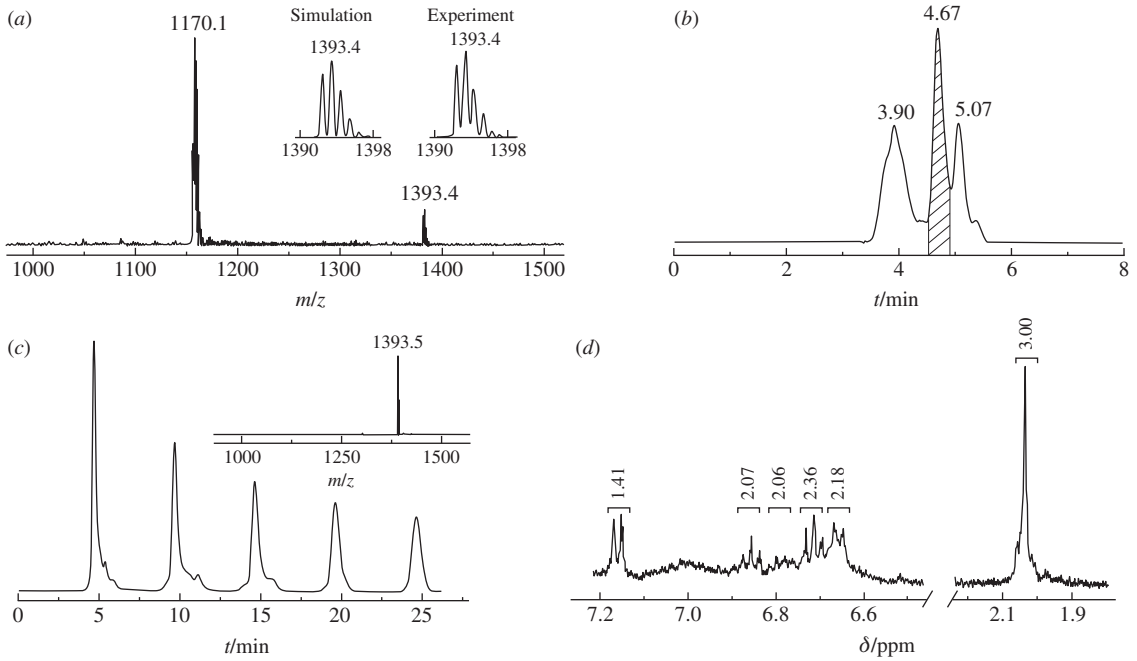


Figure 2 Characterization of $C_{60}Tol_4Ph_4$: (*a*) MS spectrum of the reaction mixture after 5 h with $C_{60}Cl_4Ph_4$:$AlCl_3$ = 1:12; (*b*) the HPLC chromatogram of $C_{60}Tol_4Ph_4$ synthesized with high excess $AlCl_3$ ($C_{60}Tol_4Ph_4$ is in the shadow part); (c) HPLC separation of $C_{60}Tol_4Ph_4$ (inset is the MS spectrum of a purified sample); and (*d*) ^{1}H NMR spectrum of $C_{60}Tol_4Ph_4$.

supports the conjecture [Figure 1(*b*)]. $C_{60}Cl_4Ph_4$ (*m*/*z* 1170.0) can be detected in the product after 2 h [Figure 1(*b*), inset] while this signal disappeared 5 h later and only $C_{60}Ph_8$ (*m*/*z* 1337.1) was detected [Figure 1(*b*)].†

Taking into account that the site-specific property of $C_{60}Cl_8$ is important for creating multifunctional materials, we attempted to replace the chlorine atoms of $C_{60}Cl_4Ph_4$ with tolyl groups using $AlCl_3$ as a catalyst. At the $AlCl_3$:$C_{60}Cl_4Ph_4$ ratio of 12:1 and a reaction time of 5 h, the MS test [Figure 2(*a*)]‡ showed that the main product was $C_{60}Cl_4Ph_4$ (*m*/*z* 1170.1) with $C_{60}Tol_4Ph_4$ (*m*/*z* 1393.4, Tol = C_6H_4Me) as a minor product. Lengthening the reaction time or raising the reaction temperature did not seriously change the composition proportion of $C_{60}Cl_4Ph_4$ to $C_{60}Tol_4Ph_4$. Increasing the amount of $AlCl_3$ did not improve the yield of $C_{60}Tol_4Ph_4$ remarkably, and, moreover, resulted in the appearance of highly arylated by-products. We finally managed to isolate $C_{60}Tol_4Ph_4$ by HPLC [Figure 2(*b*) and (*c*)]‡ for ^{1}H NMR characterization [Figure 2(*d*)].‡ The ^{1}H NMR spectrum of $C_{60}Cl_4Ph_4$ was also measured for comparison [Figure S1(*a*), Online Supplementary Materials]. The chemical shifts of H_{Ph} in $C_{60}Tol_4Ph_4$ move to upfield distinctly compared with those in $C_{60}Cl_4Ph_4$, while the UV-VIS spectra of $C_{60}Cl_4Ph_4$ and $C_{60}Tol_4Ph_4$ [Figure S1(*b*) and S1(*c*)] indicate that these compounds are isostructural. Apparently, the significant upfield shift results from the closer proximity of the benzene rings after the replacement of four chlorine atoms in $C_{60}Cl_4Ph_4$ with tolyl groups. The electron density change obtained by AM1 calculations of the two compounds supports the point (Figure S2, Online Supplementary Materials). However, only slight upfield-shift was observed in the ^{1}H NMR spectrum for the IPR-$C_{60}Cl_6$ substitution.[14] Modified IPR fullerenes with excellent properties such as antiviral activities and easy fabrication[15–17] have potential applications in medicine and materials science. Accordingly, the significant peak-shift feature in ^{1}H NMR analysis may make the modified non-IPR fullerene promising in environmental monitoring.

In conclusion, we have demonstrated that difference in the regiospecific reactivity of the two kinds of chlorine atoms in $^{\#1809}C_{60}Cl_8$ becomes a little weaker in the Friedel–Crafts reaction with $AlCl_3$ as a catalyst and $^{\#1809}C_{60}Tol_4Ph_4$ can be finally obtained by a two-step process. This facile approach makes it possible to perform the addition of diverse functional and steric-hindered groups to non-IPR fullerenes and it is fundamental for investigation of their further applications.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.01.012.

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† *Synthesis of $C_{60}Cl_4Ph_4$ and $C_{60}Ph_8$*: 10 ml of a benzene solution of $C_{60}Cl_8$ (2.8 mg) was divided evenly in two round flasks and stirred at 80 °C. Anhydrous $AlCl_3$ portions of 2 and 3.2 mg were added to the above flasks, respectively. Pure $C_{60}Cl_4Ph_4$ can be directly obtained under similar conditions with $FeCl_3$ as a catalyst.[5] Mass spectrometry followed the reactions after 2 and 5 h. Mass spectra were recorded on a Bruker Esquire HCT mass spectrometer with an APCI ion source in the negative ion mode. The dry gas temperature was 250 °C and the APCI temperature was 300 °C.

‡ *Synthesis of $C_{60}Tol_4Ph_4$*: 2.7 mg of $C_{60}Cl_4Ph_4$ was dissolved in 15 ml of toluene at 80 °C and about 4.5 mg of anhydrous $AlCl_3$ was added in an N_2 atmosphere. After 5 h, the solution was cooled to room temperature and washed with water (3×20 ml). The organic layer was dried with anhydrous $MgSO_4$. Pure $C_{60}Tol_4Ph_4$ was obtained on Buckyprep-M column (10×250 mm, flow rate, 4 ml min^{-1}). The ^{1}H NMR spectrum was recorded on a Bruker AV 400 MHz spectrometer in CD_2Cl_2 and referenced to TMS.

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