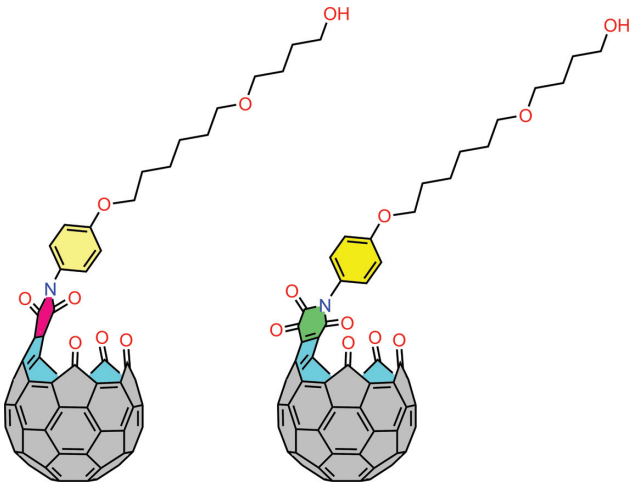
Article published online: 2020-10-21

Synthesis of Open-Cage Fullerenes with a Long Tail

Hao Zhang[a]
Jie Su[a]*
Liangbing Gan[a]*

[a] Beijing National Laboratory for Molecular Sciences, Key Laboratory of Bioorganic Chemistry and Molecular Engineering of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing, China
jie.su@pku.edu.cn, gan@pku.edu.cn



Received: 24.08.2020
Accepted after revision: 10.09.2020
DOI: 10.1055/s-0040-1718520; Art ID: om-20-0025-oa

Abstract To explore potential applications for open-cage fullerenes, we employed 4-((6-bromohexyl)oxy)aniline to react with an open-cage fullerene precursor which has an 11-membered orifice and prepared open-cage fullerenes with an 18-membered orifice. The bromo atom at the end of the hexyl chain in these open-cage compounds could be easily replaced by alkoxyl groups to further extend the linear chain. The results also show that the presence of the alkyl chain slightly changes the reactivity of the orifice-expansion reaction.

Key words fullerene, open-cage, amphiphilic

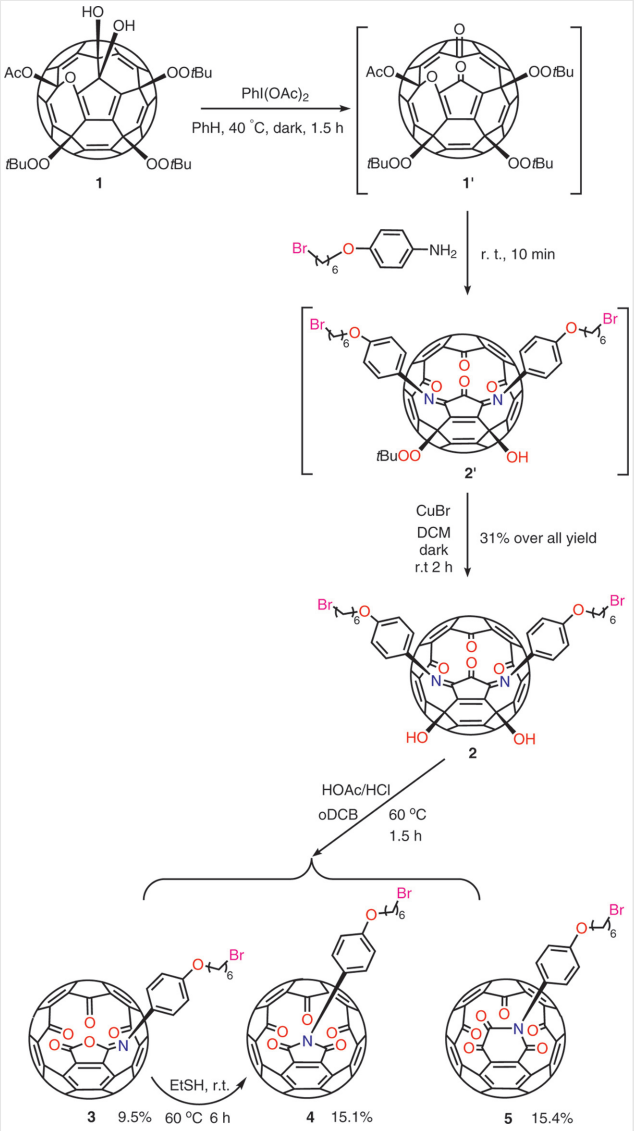
Introduction

Functionalization of fullerenes has played an important role in the exploration for their potential applications.[1] Addition of various functional groups on the spherical cage can modify their solubility,[2] redox potential,[3] absorption wavelength,[4] film formation ability,[5] and many other properties. For example, the well-known C_{60} derivative PCBM is a much better solar-cell component than pristine C_{60}.[3b] Open-cage fullerenes are a special type of fullerene derivatives with the fullerene skeleton carbon–carbon bonds selectively cleaved to form a hole. Due to the spherical nature of the fullerene cage, it is quite difficult to open the cage effectively. In spite of the difficulties, a few methods have been reported for the synthesis of open-cage fullerenes,[6] some of which have an orifice large enough to encapsulate small molecules such as water.[7]

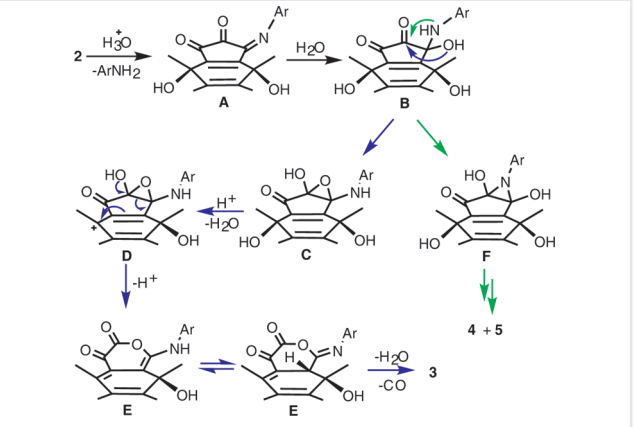
Most reported results concerning open-cage fullerenes in the literature so far have focused on the methods to open the fullerene cage and encapsulation of small molecules into the cavity of the open-cage compounds. To explore their potential applications, it is usually required to attach a suitable functional group onto the open-cage fullerene for various purposes, for example, to improve the solubility in organic solvents or water.[2] We have been working on the preparation of open-cage fullerenes with different orifice sizes and functional groups on the rim of the orifice through the fullerene mixed peroxide chemistry.[8] Based on our previous method,[9] we report here a designed synthesis of open-cage fullerenes containing a long tail, which may be used for further assembly into Langmuir–Blodgett films or spherical aggregates in water.

Results and Discussion

In our previous studies, we have used aniline and some simple aniline derivatives such as 4-methyl, 4-isopropyl, and 4-bromoanilines[9a] to make open-cage fullerenes. It is almost impossible to add other functional groups through the aniline group once it is incorporated into the open-cage derivative. In a rare case, bromination of the attached aniline was observed for an open-cage derivative in moderate yield.[10] In the present work, we synthesized 4-((6-bromohexyl)oxy)aniline following a literature method[11] and tested its reactivity in open-cage fullerene procedures. The results are mainly analogous to those of simple anilines, but there are also minor differences.



Scheme 1 Synthesis of open-cage compounds **2**, **3**, **4**, and **5**.



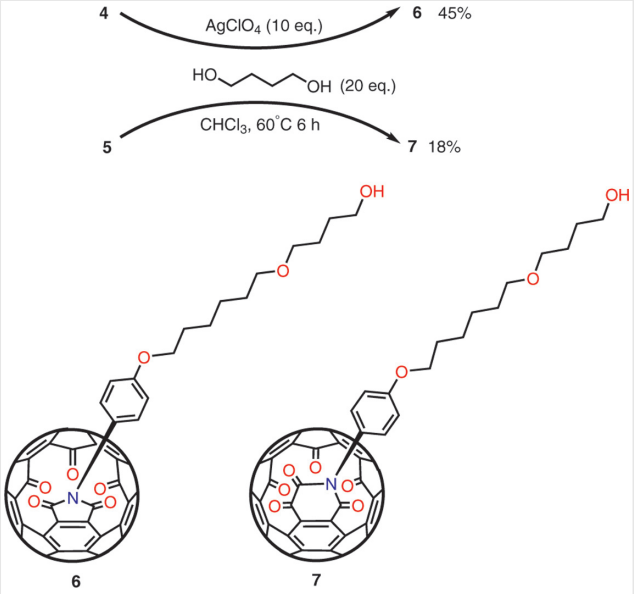
Scheme 2 Proposed mechanism for the hydrolysis reaction of **2**.

The reaction between 4-((6-bromohexyl)oxy)aniline and open-cage fullerene precursor **1** is shown in Scheme 1. Compound **1** was synthesized from C_{60} in five steps.[9a] The reaction between **1** and 4-((6-bromohexyl)oxy)aniline follows our previously reported method. Presence of the long alkyl chain slightly decreased the yield compared to the reaction with aniline (around 65%). Compound **2′** with a remaining *t*-butylperoxo group was not isolated and reduced to **2** directly from the crude products containing both **2′** and **2**.

Further hydrolysis effort converted **2** into compounds **3**, **4**, and **5** as shown in Scheme 1. In our previous study with simple aniline, we isolated compounds analogous to **4** and **5**, but without **3**. Under acidic conditions, the iminoanhydride moiety can be isomerized to the C_s symmetric imide structure. In an effort to open the iminoanhydride moiety, we found that treatment of **3** with ethanethiol (EtSH) converted **3** to **4** efficiently, in which EtSH probably opened the iminoanhydride as expected but the amino group on the resulting amide then attacked the thioester-COSEt to replace the EtS group forming the imide moiety.

The formation of **4** and **5** should follow the same mechanism as we proposed before involving intermediates **F** (Scheme 2).[9b] The reaction pattern of intermediate **B** is the key for the formation of different products. In the presence of the long alkyl chain, the hydroxyl oxygen on the aminal group was able to compete with the amino group to form intermediate **C**, which eventually led to **3** following similar processes to the formation of **4** and **5** starting from the amino nitrogen-derived intermediate **F**. The decarboxylation appears to be more efficient for the oxygen-inserted intermediate **E**. The higher yields of **4** and **5** indicate that the amino nitrogen is still more reactive than the hydroxyl oxygen in intermediate **B**.

The reactivity of the bromohexyl chain in the new open-cage fullerenes synthesized above was tested under various conditions. We first tried a few amines including piperidine and aniline. The reaction gave complex mixtures probably due to reactions on the rim of the orifice besides the expected bromo replacement reaction. The less nucleophilic alcohols such as methanol and ethanol are more selective, but phenols were not reactive enough. To attach more potentially useful functional groups, we then tested diols. The 1,2-diol did not give characterizable product. Coordination of 1,2-diol with silver ion is probably too strong, thus reduced the reactivity between the silver ion and the bromo atom. 1,4-Diol gave moderate yields when treated with compounds **4** and **5**, affording compounds **6** and **7**, respectively (Scheme 3). The same reaction between 1,4-diol and the dibromo derivative **2** gave some oligomers, which were not fully characterized.



Scheme 3 Further reaction of **4** and **5** to form compounds **6** and **7**.

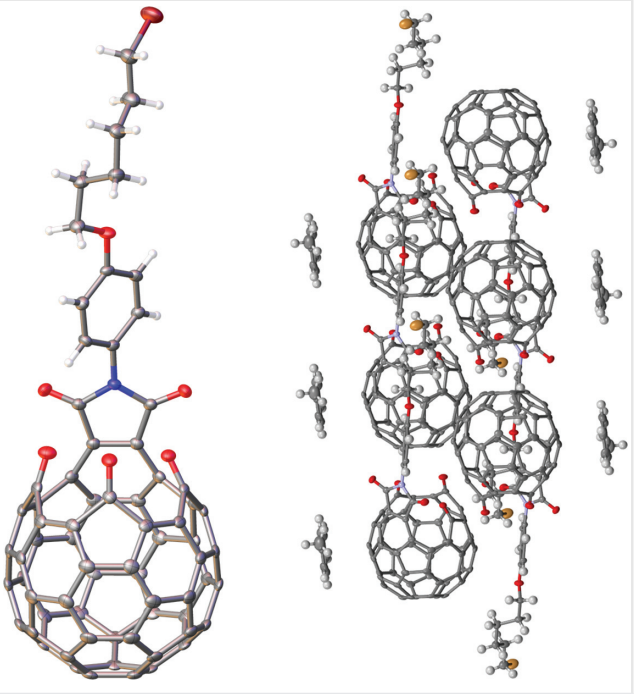


Figure 1 Single-crystal X-ray structures of compound **4** and the linear packing in the crystal (right). Ellipsoids are set at 50% probability. Color scheme: C grey, N blue, O red, and H white.

Spectroscopic data of the new compounds agree with the structures depicted in the above schemes. Both compounds **2** and **4** are C_s symmetric. As expected, their ^{13}C NMR spectra showed 35 signals in the sp^2 carbon region from 114 ppm to 186 ppm for the sp^2 cage carbons and the phenyl carbons. Comparison of the carbonyl signals of **2** and **4** indicates that the signal at 185 ppm is due to the two equivalent carbonyl carbons on the rim of the orifice. The signal at 184 ppm is due to the other carbonyl carbon between these two carbonyl groups on the rim. The signal at 175 ppm in **2** is due to the carbonyl between the two imino groups, which is absent in the imide compound **4**. Other compounds are all C_1 symmetric and it is not possible to assign any signals conclusively.

The structure of compound **4** is also confirmed by single crystal X-ray diffraction analysis. The crystals were obtained from its toluene solution (Figure 1). The solvent toluene molecule in the crystal formed weak π–π interaction with the fullerene cage. The aniline ring also formed weak π–π interaction with an adjacent fullerene cage. The intermolecular head to tail interactions result in linear arrangements in the layered crystal packing. The alkyl group shows a zig-zag orientation along the 1,4-axis of the phenyl group. The angle between the imide five-membered plane and the aniline plane is 45.8°. The double bonds conjugated with two carbonyl groups on the rim are the shortest double bond on the cage at 1.37 Å. Single bonds on the rim (more than 1.5 Å) are also longer than other single bonds on the cage (around 1.4 Å).

Conclusions

The aniline derivative with a bromohexyl chain has been shown to be able to expand the orifice of open-cage fullerene precursors just like simple anilines. The presence of the bromohexyl groups slightly modifies the reactivity pattern and allows isolation of the less stable iminoanhydride compound **3**. The bromo atom at the end of the alkyl chain showed good reactivity toward alcohols. Presence of the hydrophilic moiety in the tails of open-cage compounds **6** and **7** renders these compounds amphiphilic and allows potential applications in molecular self-assembly.[5,12]

Experimental Section

All reagents and solvents were used as received. The reactions were carried out under atmospheric conditions. The NMR spectra were obtained at 25 °C with 400, 500, and 600 MHz spectrometers (^{1}H and ^{13}C NMR spectra for the same compounds were obtained with different spectrometers and different solvents in some cases). Chemical shifts are given in ppm relative to $CDCl_3$. ESI-FT-ICR-HRMS spectra were recorded in positive mode. UV/vis spectra are measured with PerkinElmer Lambda 3600 UV/vis spectrometer. Chromatographic purifications were carried out

with silica gel of mesh 200–300. Known compounds were characterized by comparison of their ^{1}H NMR data with literature data as cited.

Note: common impurities such as residue solvent toluene and grease from silica gel are sometimes impossible to be removed from the fullerene derivatives by routine flash column chromatography. Further purification by a diffusion–precipitation procedure was usually required to obtain pure samples. The diffusion–precipitation solvents are CS_2/EtOH or $CHCl_3$/EtOH.

Procedures

Preparation of Compound 2

Compound **1** (300.0 mg, 0.27 mmol) was dissolved in dry benzene, 132.2 mg $PhI(OAc)_2$ (0.41 mmol, 1.5 eq.) was added, and the resulting solution was stirred for 1 h at 40 °C. After **1** converted into a less polar orange compound **1′**, freshly prepared compound 4-((6-bromohexyl)oxy)aniline (about 731.0 mg, 2.70 mmol), which can be easily synthesized from *p*-nitrophenol,[11] was added resulting in a black solution. The flask was cooled to room temperature and stirred for 10 min. Purification of the crude solution by column chromatography (toluene:EtOAc = 100:1) afforded a mixture of **2** and **2′**, then the mixture was washed with 200 mL hydrochloric acid (1 M) for three times and dried over Na_2SO_4 and concentrated under vacuum.

The obtained mixture above was dissolved into 150 mL CH_2Cl_2 followed by addition of 15 µL water and stirred at room temperature for 30 min. CuBr (105 mg, about 5 eq.) was added into the solution and stirred for another 2 h at room temperature until complete conversion of **2′** to the symmetrical compound **2**. Solvents were removed under vacuum and the crude residue was purified by column chromatography (toluene:EtOAc = 100:1) to afford 114.4 mg black solid **2** (0.084 mmol, 31.1%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 2H), 7.72 (d, J = 8.8 Hz, 4H), 6.99 (d, J = 8.8 Hz, 4H), 4.04 (dt, J = 6.3, 2.5 Hz, 4H), 3.45 (t, J = 6.8 Hz, 4H), 1.94–1.91 (m, 4H), 1.86–1.83 (m, 4H), 1.55–1.53 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.15 (*C*O), 184.08 (*C*O), 175.53, 159.70, 154.35, 149.89, 149.71, 149.67, 149.54, 149.51, 149.42, 148.36, 148.35, 148.26, 148.02, 147.18, 146.48, 146.02, 145.97, 145.55, 144.98, 144.87, 144.46, 144.41, 143.55, 143.53, 143.31, 142.71, 140.64, 138.51, 136.48, 136.42, 126.98, 126.67, 114.32, 78.08, 68.16 (CH_2), 33.98 (CH_2), 32.85 (CH_2), 29.20 (CH_2), 28.08 (CH_2), 25.47 (CH_2). ESI-FT-ICR-HRMS-positive $C_{84}H_{35}Br_2N_2O_8$ (M + H$^+$): calculated 1357.0755, found 1357.0715.

Preparation of Compounds 3, 4, and 5

Compound **2** (191.4 mg, 0.15 mmol) was dissolved in 100 mL *o*DCB followed by addition of 500 mL HOAc and 80 mL of hydrochloric acid (12 M). The reaction mixture was heated to 60 °C and left to stir for about 1.5 h until the complete conversion of compound **2**. The crude solution was cooled to room temperature and washed with water (300 mL) for three times. The organic layer was dried over Na_2SO_4, and then separated by column chromatography immediately (toluene:EtOAc = 20:1) to afford 14.1 mg black solid compound **3** (0.018 mmol, 9.5%), 22.5 mg brown solid compound **4** (0.021 mmol, 15.1%), and 23.6 mg brown solid compound **5** (0.22 mmol, 15.4%) sequentially.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 4.08 (t, J = 6.4 Hz, 4H), 3.48 (t, J = 6.8 Hz, 4H), 1.98–1.93 (m, 2H), 1.90–1.85 (m, 2H), 1.58–1.56 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.93 (*C*O), 185.92 (*C*O), 185.75, 183.99, 163.01, 158.56, 150.65, 150.57, 150.19, 149.88, 149.78, 149.73, 149.53, 149.06, 147.00, 146.98, 146.93, 146.88, 146.85, 146.55, 146.47, 146.46, 146.44, 146.32, 146.15, 145.92, 145.88, 145.76, 145.57, 143.87, 143.86, 143.74, 143.60, 143.58, 143.42, 143.14, 143.07, 143.06, 142.88, 141.93, 141.86, 138.32, 137.94, 137.85, 137.56, 137.33, 137.21, 136.46, 136.06, 135.88, 133.70, 132.88, 132.19, 128.56, 127.78, 127.57, 127.36, 115.07, 68.19 (CH_2), 34.02 (CH_2), 32.90 (CH_2), 29.28 (CH_2), 28.15 (CH_2), 25.51 (CH_2). ESI-FT-ICR-HRMS-positive $C_{71}H_{17}BrNO_6$ (M + H$^+$): calculated 1058.0234, found 1058.0240.

Compound 4

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.7 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 4.13 (t, J = 6.3 Hz, 2H), 3.49 (t, J = 6.8 Hz, 2H), 2.02–1.95 (m, 2H), 1.94–1.89 (m, 2H), 1.62–1.57 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 185.72 (*C*O), 184.18 (*C*O), 165.36, 159.27, 150.51, 150.18, 149.78, 149.68, 149.50, 148.87, 147.14, 147.04, 146.82, 146.78, 146.47, 146.30, 146.19, 145.87, 143.94, 143.86, 143.78, 143.67, 143.26, 143.09, 142.01, 138.16, 137.89, 137.66, 133.67, 132.04, 131.00, 128.98, 128.31, 125.20, 115.55, 68.23 (CH_2), 34.04 (CH_2), 32.94 (CH_2), 29.29 (CH_2), 28.17 (CH_2), 25.55 (CH_2). ESI-FT-ICR-HRMS-positive $C_{71}H_{17}BrNO_6$ (M + H$^+$): calculated 1058.0234, found 1058.0234; $C_{71}H_{20}BrN_2O_6$ (M + NH_4^+): calculated 1075.0500, found 1075.0501.

Crystals of compound **4** suitable for single-crystal X-ray diffraction were obtained from slow evaporation of toluene. Crystal data for $C_{78}H_{24}BrNO_6$ (M = 1150.89 g/mol): triclinic, space group P-1 (no. 2), a = 10.1787(2) Å, b = 13.1456(3) Å, c = 17.4033(3) Å, α = 93.358(2)°, β = 91.417(2)°, γ = 95.437(2)°, V = 2313.12(8) Å^3, Z = 2, T = 180.00(10) K, μ (Mo Kα) = 0.962 mm^{-1}, D_{calc} = 1.652 g/cm^3, 29603 reflections measured (4.014° ≤ 2Θ ≤ 54.968°), 10605 unique (R_{int} = 0.0295, R_{sigma} = 0.0398), which were used in all calculations. The final R_1 was 0.0480 ($I > 2\sigma(I)$) and wR_2 was 0.1303 (all data). Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC-1888266.

Compound 5

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 2H), 7.22 (d, J = 8.2 Hz, 2H), 4.11 (t, J = 6.2 Hz, 2H), 3.47 (t, J = 6.8 Hz, 2H), 1.99–1.93 (m, 2H), 1.91–1.90 (m, 2H), 1.58 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 186.49 (*C*O), 186.45 (*C*O), 183.74 (*C*O), 175.99 (*C*O), 162.33 (*C*O), 159.70, 158.30, 150.46, 150.42, 150.10, 149.80, 149.78, 149.66, 149.63, 149.51, 149.45, 148.90, 147.38, 147.08, 147.04, 147.01, 146.95, 146.94, 146.58, 146.52, 146.35, 146.30, 146.12, 145.95, 145.70, 145.63, 143.88, 143.87, 143.84, 143.69, 143.45, 143.36, 143.34, 142.85, 142.77, 142.29, 141.81, 141.73, 139.39, 138.69, 138.01, 137.96, 137.91, 133.75, 132.35, 132.27, 131.73, 131.58, 131.05, 130.66, 130.40, 130.12, 126.82, 115.44, 68.10 (CH_2), 34.05 (CH_2), 32.90 (CH_2), 29.29 (CH_2), 28.13 (CH_2), 25.55 (CH_2). ESI-FT-ICR-HRMS-positive $C_{72}H_{17}BrNO_7$ (M + H$^+$): calculated 1086.0183, found 1086.0180. ESI-FT-ICR-HRMS-positive $C_{72}H_{20}BrN_2O_7$ (M + NH_4^+): calculated 1103.0448, found 1103.0455.

Preparation of Compound 6

Compound **4** (17.1 mg, 0.016 mmol) was dissolved into 10 mL $CHCl_3$, 36.4 mg of $AgClO_4{\cdot}H_2O$ (0.16 mmol, 10 eq.), and 28.7 µL of butanediol (0.33 mmol, 20 eq.) was added, then the resulting solution was heated up to 60 °C and stirred for 6 h. The crude solution was cooled to room temperature and washed with 10 mL water for three times. The organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude was purified by column chromatography (CH_2Cl_2:EtOAc = 3:1) to afford 7.7 mg black solid compound **6** (0.0072 mmol, 44.6%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (d, J = 8.7 Hz, 2H), 7.25 (d, J = 8.7 Hz, 2H), 4.14 (t, J = 6.4 Hz, 2H), 3.68 (t, J = 5.6 Hz, 2H), 3.51 (dt, J = 6.8, 4.0 Hz, 4H), 1.93–1.89 (m, 2H), 1.73–1.68 (m, 6H), 1.60 (d, J = 8.0 Hz, 2H), 1.51 (d, J = 7.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 185.74 (*C*O), 184.20 (*C*O), 165.41, 159.37, 150.51, 150.18, 149.78, 149.69, 149.50, 147.14, 147.03, 146.83, 146.79, 146.48, 146.31, 146.20, 145.88, 143.94, 143.86, 143.79, 143.68, 143.27, 143.10, 142.02, 138.17, 137.90, 137.65, 133.69, 132.04, 131.01, 128.97, 128.32, 115.56, 71.16 (CH_2), 71.08 (CH_2), 68.32 (CH_2), 62.99 (CH_2), 30.62 (CH_2), 29.74 (CH_2), 29.35 (CH_2), 27.19 (CH_2), 26.07 (CH_2), 26.06 (CH_2). ESI-FT-ICR-HRMS-positive $C_{75}H_{26}NO_8$ (M + H$^+$): calculated 1068.1653, found 1068.1628.

Preparation of Compound 7

Compound **5** (31.2 mg, 0.029 mmol) was dissolved into 15 mL $CHCl_3$, 64.8 mg of $AgClO_4{\cdot}H_2O$ (0.28 mmol, 10 eq.), and 51.0 µL of butanediol (0.56 mmol, 20 eq.) was added, then the resulting solution was heated up to 60 °C and stirred for 6 h. Following the work-up procedure for compounds **6**, compound **7** was obtained as a black solid (5.5 mg, 0.0050 mmol, 17.5%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 2H), 7.23 (s, 2H), 4.12 (t, J = 6.2 Hz, 2H), 3.67 (s, 2H), 3.50 (t, J = 5.8 Hz, 4H), 2.55 (s, 1H), 1.92–1.85 (m, 2H), 1.71–1.67 (m, 4H), 1.57 (s, 4H), 1.49 (d, J = 6.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 186.50 (*C*O), 186.46 (*C*O), 183.74 (*C*O), 176.05, 162.40, 159.82, 158.36, 150.48, 150.44, 150.12, 149.82, 149.81, 149.68, 149.66, 149.54, 149.47, 148.93, 147.40, 147.11, 147.06, 147.04, 146.97, 146.96, 146.61, 146.54, 146.36, 146.32, 146.14, 145.99, 145.73, 145.67, 143.90, 143.87, 143.72, 143.47, 143.38, 143.37, 142.87, 142.79, 142.32, 141.85, 141.83, 141.78, 139.45, 138.74, 138.05, 138.01, 137.93, 133.78, 132.39, 132.30, 131.77, 131.62, 131.05, 130.68, 130.36, 130.17, 126.72, 115.48, 71.16 (CH_2), 71.07 (CH_2), 68.20 (CH_2), 62.98 (CH_2), 30.63 (CH_2), 29.74 (CH_2), 29.36 (CH_2), 27.18 (CH_2), 26.07 (CH_2). ESI-FT-ICR-HRMS-positive $C_{76}H_{26}NO_9$ (M + H$^+$): calculated 1096.1602, found 1096.1574.

Funding Information

This work has been founded by National Natural Science Foundation of China (NNSFC: 21672009 and 21871015) and by Beijing National Laboratory for Molecular Sciences (BNLMS-CXXM-201904).

Supporting Information

Supporting information for this article is available online at http://doi.org/10.1055/s-0040-1718520.

References

(1) (a) Hirsch, A.; Brettreich, M. Fullerenes: Chemistry and Reactions. Wiley-VCH: Weinheim; **2005**. (b) Thilgen, C.; Diederich, F. *Chem. Rev.* **2006**, *106*, 5049.

(2) For example the "fullerene sugar balls": (a) Nierengarten, J.-F.; Iehl, J.; Oerthel, V.; Holler, M.; Illescas, B. M.; Munoz, A.; Martin, N.; Rojo, J.; Sanchez-Navarro, M.; Cecioni, S.; Vidal, S.; Buffet, K.; Durka, M.; Vincent, S. P. *Chem. Commun.* **2010**, *46*, 3860. (b) Muñoz, A.; Sigwalt, D.; Illescas, B. M.; Luczkowiak, J.; Rodríguez-Perez, L.; Nierengarten, I.; Holler, M.; Remy, J.-S.; Buffet, K.; Vincent, S. P.; Rojo, J.; Delgado, R.; Nierengarten, J.-F.; Martín, N. *Nat. Chem.* **2016**, *8*, 50. (c) Ramos-Soriano, J.; Reina, J. J.; Illescas, B. M.; de la Cruz, N.; Rodriguez-Perez, L.; Lasala, F.; Rojo, J.; Delgado, R.; Martin, N. S. *J. Am. Chem. Soc.* **2019**, *141*, 15403.

(3) (a) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978. (b) Hummelen, J. C.; Knight, B. W.; Lepeq, F.; Wudl, F.; Yao, J.; Wilkins, C. L. *J. Org. Chem.* **1995**, *60*, 532. (c) He, Y.; Chen, H. Y.; Hou, J.; Li, Y. *J. Am. Chem. Soc.* **2010**, *132*, 1377. (d) Umeyama, T.; Imahori, H. *Acc. Chem. Res.* **2019**, *52*, 2046.

(4) (a) Zheng, M.; Li, F.; Shi, Z.; Gao, X.; Kadish, K. M. *J. Org. Chem.* **2007**, *72*, 2538. (b) Li, Y. B.; Xu, D.; Gan, L. B. *Angew. Chem. Int. Ed.* **2016**, *55*, 2483. (c) Kosaya, M. P.; Rybalchenko, A. V.; Lukonina, N. S.; Mazaleva, O. N.; Ioffe, I. N.; Markov, V. Y.; Troyanov, S. I.; Sidorov, L. N.; Tamm, N. B.; Goryunkov, A. A. *Chem. Asian J.* **2018**, *13*, 1920. (d) Li, D.; Li, Z. J.; He, F. G.; Geng, C.; Gao, X. *J. Org. Chem.*

2019, *84*, 14679. (e) Liu, K. Q.; Wang, J. J.; Yan, X. X.; Niu, C.; Ang, G. W. *Chem. Sci.* **2020**, *11*, 384.

(5) (a) Jehoulet, C.; Obeng, C.; Kim, Y. T.; Zhou, F.; Bard, A. J. *J. Am. Chem. Soc.* **1992**, *114*, 4237. (b) Zhou, D. J.; Gan, L. B.; Luo, C. P.; Huang, C. H.; Yao, G. Q.; Zhao, X. S.; Liu, Z. F.; Xia, X. H.; Zhang, B. *J. Phys. Chem.* **1996**, *100*, 3150. (c) Mezour, M. A.; Choueiri, R. M.; Lukoyanova, O.; Lennox, R. B.; Perepichka, D. F. *Nanoscale* **2016**, *8*, 16955. (d) Liu, J.; Wang, Y.; Jiang, P.; Tu, G. *ACS Omega* **2020**, *5*, 1336.

(6) (a) Murata, M.; Murata, Y.; Komatsu, K. *Chem. Commun.* **2008**, *46*, 6083. (b) Vougioukalakis, G. C.; Roubelakis, M. M.; Orfanopoulos, M. *Chem. Soc. Rev.* **2010**, *39*, 817. (c) Gan, L.; Yang, D.; Zhang, Q.; Huang, H. *Adv. Mater.* **2010**, *22*, 1498.

(7) Shi, L. J.; Gan, L. B. *J. Phys. Org. Chem.* **2013**, *26*, 766.

(8) (a) Gan, L. *Chem. Rec.* **2015**, *15*, 189. (b) Gan, L. B. *Chin. J. Chem.* **2018**, *36*, 991. (c) Gan, L. *Acc. Chem. Res.* **2019**, *52*, 1793.

(9) (a) Zhang, Q.; Jia, Z.; Liu, S.; Zhang, G.; Xiao, Z.; Yang, D.; Gan, L.; Wang, Z.; Li, Y. *Org. Lett.* **2009**, *11*, 2772. (b) Zhang, H.; Xu, L.; Gan, L. *ChemPlusChem* **2017**, *82*, 1002.

(10) Xiao, Z.; Yao, J.; Yang, D.; Wang, F.; Huang, S.; Gan, L.; Jia, Z.; Jiang, Z.; Yang, X.; Zheng, B.; Yuan, G.; Zhang, S.; Wang, Z. *J. Am. Chem. Soc.* **2007**, *129*, 16149.

(11) Tritto, E.; Chico, R.; Sanz-Enguita, G.; Folcia, C. L.; Ortega, J.; Coco, S.; Espinet, P. *Inorg. Chem.* **2014**, *53*, 3449.

(12) (a) Homma, T.; Harano, K.; Isobe, H.; Nakamura, E. *Angew. Chem. Int. Ed.* **2010**, *49*, 1665. (b) Zhang, G.; Liu, Y.; Liang, D. H.; Gan, L. B.; Li, Y. L. *Angew. Chem. Int. Ed.* **2010**, *49*, 5293. (c) Kraft, A.; Roth, P.; Schmidt, D.; Stangl, J.; Müller-Buschbaum, K.; Beuerle, F. *Chemistry* **2016**, *22*, 5982. (d) Nitta, H.; Harano, K.; Isomura, M.; Backus, E. H. G.; Bonn, M.; Nakamura, E. *J. Am. Chem. Soc.* **2017**, *139*, 7677.