JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

Selective Addition of Secondary Amines to C_{60}: Formation of Penta- and Hexaamino[60]fullerenes

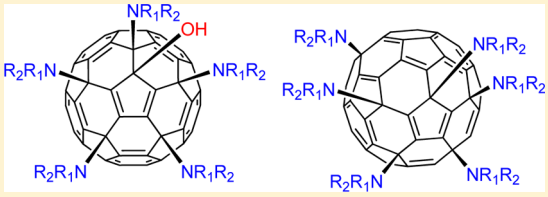
Yanbang Li[†] and Liangbing Gan*[,†,‡]

[†]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 100871, China

[‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032, China

Supporting Information

ABSTRACT: Secondary amines are well-known to add to [60]fullerene to form the tetraamino epoxy adduct $C_{60}(O)(NR_1R_2)_4$ under both photolysis and thermal conditions in the presence of oxygen. We have now found that pentaamino hydroxyl adduct $C_{60}(OH)(NR_1R_2)_5$ and hexaamino adduct $C_{60}(NR_1R_2)_6$ can be formed as the major products in the dark in the presence of oxygen. Key steps of the reaction mechanism probably involve repeated oxygen oxidation of the radical ion pair between fullerene and amines.



Addition of amines to fullerenes is one of the most intensively studied fullerene reactions.[1] Many aminofullerenes have been prepared for their potential applications.[2] Because of the poor selectivity, most of the reported aminofullerenes are complex mixtures of multiadducts. Isomerically pure amino adducts are relatively rare compared to other types of fullerene derivatives. Some primary amines add to C_{60} to form the aziridinofullerenes or azafulleroid in the presence of added oxidants.[3] Aliphatic polyamines, such as diethylenetriamine, acted as hydrogenation reagents to form C_{3v} $C_{60}H_{18}$ at elevated temperatures.[4] Secondary amines such as piperazine[5] and azacrown ether[6] can react with fullerene to selectively form the corresponding monoadduct. Anilides, benzamides, carbamates, and sulfonates react with C_{60} to form various [60]fullerene-fused heterocyclic products through metal-assisted oxidation reactions.[7] Tertiary amines react with fullerenes at the carbon atom(s) next to the amino nitrogen atom to form fulleropyrrolidines[8] or 1,2-dihydrofullerenes.[9] Copper-catalyzed C−H amination of monofunctionalized hydrofullerenes results in 1,4-difunctional fullerenes with an amino group.[10]

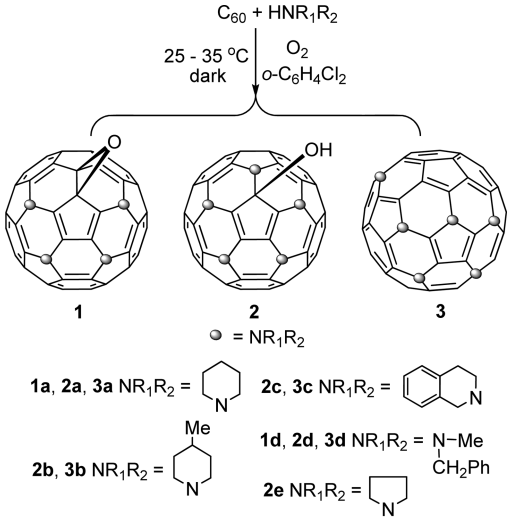
Isomerically pure multiamino fullerene adducts are mainly limited to tetraamino epoxy [60]fullerenes, which have been prepared with secondary amines under different conditions.[11] Amino adducts with more than four amino groups are still quite rare. Nakamura et al. isolated a small amount of the pentaamino hydroxyl [60]fullerene adduct $C_{60}(OH)(N(CH_2)_3)_5$ for the azetine reaction, which was not fully characterized.[11d] Troshin et al. reported the pentaamino adduct $C_{60}(X)(amine)_5$ (X = Cl or H) through the reaction between $C_{60}Cl_6$ and piperazine hydrochloric acid salts.[2c] We have reported aminooxahomofullerene adducts $C_{60}(O)_4(OH)(amine)_5$[12] and tetraamino epoxy adduct $C_{60}(O)(MeNCH_2COOMe)_4$.[3c] As a continuation of our interest in fullerene multiadducts, here we report the one-step preparation of penta- and hexaamino[60]fullerenes by treating C_{60} with secondary amines in the presence of oxygen in the dark.

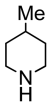
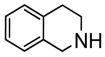
Secondary amines have been reported to react with C_{60} to form tetraamino epoxy [60]fullerenes under both light and dark conditions in the presence of oxygen.[11] In an effort to prepare the epoxy adduct, we found that the pentaamino hydroxyl adduct **2** and hexaamino adduct **3** could be obtained as the major products under optimized conditions (Scheme 1, table). Both the ratio between the reactants and the concentration of the reaction mixture are very important to give good selectivity. To avoid the involvement of singlet oxygen, the reaction was conducted in the dark. Upon addition of the amine, there was an immediate color change, but formation of compounds **2** and **3** was relatively slow and could be easily followed by TLC. The tetraamino epoxy adduct **1** was detected as an intermediate, which slowly changed to the pentaamino hydroxyl adduct **2**. Compound **2** can be stored for several weeks without any noticeable change, but compound **3** slowly decomposes in a $CDCl_3$ or toluene solution over a week.

For the piperidine and 4-methylpiperidine reactions, both compounds **3a** and **3b** are actually inseparable regioisomers. To improve the regioselectivity, we then used the more sterically demanding 1,2,3,4-tetrahydroisoquinoline. As expected, the hexaadduct **3c** could be isolated as a single isomer. In this case, 3 times more amines are needed than in the piperidine reaction. This reaction appeared to be the best among the amines shown in the table in Scheme 1 in terms of both total yields and regioselectivity. The bulky *N*-methylbenzylamine reacted similarly to form isomerically pure **2d** and **3d** when an even larger excess of the amine (4 times more than in the piperidine reaction) was used. Interestingly, compound **4** with a fullerene-fused oxazolidine ring was isolated as a minor product. It may

Received: July 15, 2014
Published: August 21, 2014

Scheme 1

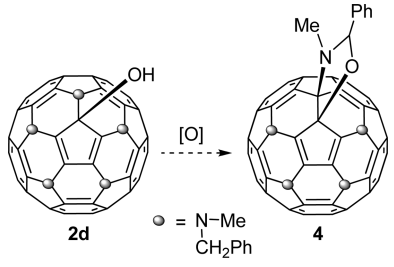


	Amine	Ratio	Time (Day)	Yields % 1	2	3
a		1:30	4	8	21	42[a]
b		1:30	5	-[b]	15	30[a]
c		1:90	1	-	35	40
d		1:120	4	-	24	44
		1:30	4	38	-	-
e		1:30	2	-	17	-

[a]Mixture of two regioisomers. [b]A hyphen means a trace amount.

be due to oxidative intramolecular cyclization of compound **2d** (Scheme 2).[13] The amount of amines played a key role in the selectivity of this reaction. The tetraamino epoxy adduct **1d** was the major product with a molar ratio of 1:30 between C_{60} and amine. The less bulky pyrrolidine yielded the pentaamino hydroxyl adduct **2e** as the only isolable product. We failed to extend the reaction to other aliphatic amines, including morphaline and *N*-methylpiperazine. These amines gave complicated mixtures under the conditions described here.

Scheme 2



All the compounds shown in the table in Scheme 1 showed the expected molecular ion signal as the most intensive or the only signal on the ESI-HRMS spectrum. The presence of the amino groups appears to facilitate ESI-MS detection. The ^{1}H NMR spectra are relatively broad for all the compounds. The ^{13}C NMR spectra showed that as the amines become bulkier, rotation of the addends is severely hindered. For C_s symmetric compounds **2a**–**e**, the pyrrolidine adduct **2e** showed sharp signals for all the carbon atoms on the ^{13}C NMR spectrum. The piperidine adducts **2a** and **2b** showed broadened signals for the three fullerene skeleton carbons with the largest chemical shifts around 153, 152, and 150 ppm. As expected, the sp^3 fullerene skeleton carbons connecting the addends appeared as four signals reflecting the C_s symmetry for all three compounds.

Even though **2c** and **2d** have the same addition pattern as **2a**, **2b**, and **2e**, their NMR spectra showed C_1 symmetry. For example, the ^{1}H NMR spectrum of **2d** showed five methyl signals. The ^{13}C NMR spectrum of **2d** showed six sp^3 fullerene skeleton carbon signals. Nevertheless, the chemical shifts of these six sp^3 fullerene skeleton carbon signals are quite close to those of compounds **2a** and **2b**. The differences are within 0.7 ppm for the corresponding signals. In addition, the three fullerene skeleton carbons with the largest chemical shifts around 153, 152, and 150 ppm mentioned above for **2a** and **2b** now appear as six signals. These data suggest that the apparent C_1 symmetry of **2c** and **2d** is due to hindered rotation of the addends, not the addition pattern. Compounds **2a**–**e** are all orange, a fact that also strongly supports the same structural assignment. As demonstrated for many fullerene adducts, any change in the addition pattern will result in a different conjugation system on the cage surface, and thus a clear color change.

Compounds **3c** and **3d** showed a similar C_1 symmetric pattern with sharp ^{13}C NMR signals. This phenomenon is in agreement with the fact that addends in **3c** and **3d** are further apart than their corresponding pentaamino adducts **2c** and **2d**. The ^{13}C NMR spectrum of compound **3a** showed the presence of two isomers in an ~4:1 ratio, with the major isomer having sp^3 fullerene skeleton signals similar to those of **3c** and **3d**. The minor signal showed four sp^3 fullerene skeleton signals at 71.18, 72.97, 74.01, and 75.17 ppm, indicating an addition pattern with C_s symmetry similar to that in compound **2a**.

Comparison of the HRMS and NMR spectra between compounds **2d** and **4** clearly indicates the formation of the oxazolidine ring at the benzyl position in compound **4**. Five methyl and five methylene groups can be easily identified for **2d**. At chemical shifts comparable to those of **2d**, there are five methyl and four methylene groups for **4** on the ^{1}H and ^{13}C NMR spectra. The DEPT spectrum of **4** showed the expected CH signal at 97.6 ppm. The tetraamino epoxy adduct **1d** showed the expected signals for C_s symmetry on the ^{1}H and ^{13}C NMR spectra.

The structures of compounds **2b** and **2e** are further confirmed by single-crystal diffraction analysis (Figure 1). Both crystals were obtained from slow evaporation of their CS_2/EtOH solution. The two structures show a number of similarities. Piperidine and pyrrolidine groups in the two compounds are well-ordered around a central pentagon of the fullerene cage, exhibiting pseudo-C_5 symmetry if the hydroxyl

dx.doi.org/10.1021/jo5015867 | J. Org. Chem. 2014, 79, 8912–8916

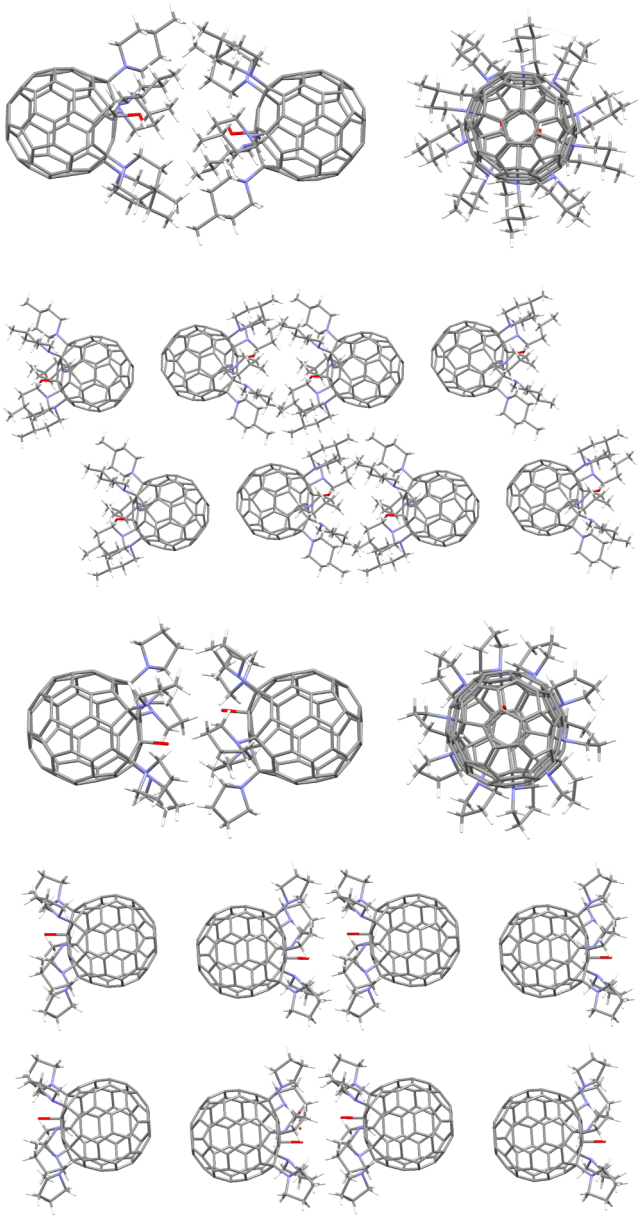


Figure 1. Two views of the dimeric structure and crystal packings (one layer is shown) for compounds **2b** (top half) and **2e** (bottom half). For the sake of clarity, solvent molecules in **2e** were not drawn. Color scheme: gray for C, blue for N, red for O, and white for H.

group is neglected. The hydroxyl group is disordered over three adjacent carbons on the central pentagon for **2b** and over four adjacent carbons on the central pentagon for **2e**. Both compounds show head-to-head and tail-to-tail linear polymeric structures in the crystal packing. Adjacent linear chains in **2b** are slightly slipped, whereas those in **2e** are better aligned. The distance between the centers of the central cyclopentadienyl pentagon of the two adjacent molecules is 8.903 Å for **2b** and 6.737 Å for **2e**, apparently because of the different sizes of the 4-methylpiperidine and the pyrrolidine rings. The interaction distances between the fullerene cages in the linear chain are around 3.3 Å for both compounds. This crystal packing pattern is different from the head-to-tail shuttle cork pattern observed by Nakamura et al. for their cyclopentadienyl adducts.[14]

Slightly different mechanisms have been suggested to explain the formation of tetraamino epoxy [60]fullerene under photolysis and in the dark.[11] Singlet oxygen is the active oxidant under photolysis. For the dark reaction presented here, ground state oxygen should act as the oxidant. The mechanism[15] should be basically the same as that proposed by Nakamura et al. for the addition of secondary amines to C_{60} in a mixture of DMSO and chlorobenzene that gave the tetraamino epoxy [60]fullerene as the major product.[11d] The reaction conditions used in our study are quite similar to Nakamura's conditions except that we used a large excess of secondary amines and *o*-dichlorobenzene as the solvent.

In summary, this work reports the selective formation of penta- and hexaamino[60]fullerenes through the direct reaction of secondary amines with C_{60} in the presence of oxygen in the dark. The results strongly support the oxygen-induced addition of amines to C_{60} through oxidation of the initially formed radical ion pair between C_{60} and a secondary amine. The stable pentaamino hydroxyl adduct should behave like the tetraamino epoxy adduct in terms of their potential applications.

EXPERIMENTAL SECTION

All reagents were used as received. The NMR spectra were recorded at 25 °C with 400, 500, and 600 MHz spectrometers (^{1}H and ^{13}C NMR spectra for the same compound were obtained with different spectrometers in some cases). Chemical shifts are given in parts per million relative to TMS or $CDCl_3$ (for ^{13}C NMR). The CS_2:$CDCl_3$ volume ratio is around 10:1 for ^{13}C NMR spectra. Chromatographic purifications were conducted with silica gel of mesh 200−300.

Compounds 2a and 3a. To a solution of C_{60} (72 mg, 0.1 mmol) in 10 mL of dichlorobenzene was added 30 equiv of piperidine (0.296 mL, 3.0 mmol). The resulting solution was stirred at rt for 4 days. The reaction was terminated upon confirmation of nearly complete conversion of C_{60} and the initially formed **1a**. The solution was chromatographed on a silica gel column eluting with petroleum ether to remove dichlorobenzene. Eluting with a petroleum ether/toluene mixture (1:1) gave the first red band as compound **2a** (24 mg, 0.021 mmol, 21%). Eluting with a toluene/ethyl acetate mixture (40:1) gave the second red band as compound **1a** (9 mg, 0.007 mmol, 8%) and the third black band as compound **3a** (52 mg, 0.0425 mmol, 42%).

2a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92−3.91 (m, 2H), 3.18−3.07 (m, 15H), 2.63−2.58 (m, 2H), 2.31−2.29 (m, 5H), 1.70−1.51 (m, 26H); ^{13}C NMR (126 MHz, CS_2/$CDCl_3$) (all signals represent 2C except as noted) δ 152.83, 152.41, 150.28, 148.72, 148.47, 148.38, 148.10, 148.05, 147.98, 147.79 (1C), 147.39, 147.09 (1C), 147.03, 146.96, 146.56, 145.46, 144.97, 144.30, 144.14, 143.86, 143.76, 143.63, 143.27, 143.03, 142.76, 142.58, 141.56, 141.09, 81.04 (1C), 73.83, 73.32 (1C), 71.09, 53.62, 51.41 (4C), 51.15 (4C), 27.49, 27.19 (4C), 27.13 (4C), 25.04, 24.89, 24.23 (1C); ESI-FT-ICR-HRMS-positive $C_{85}H_{52}N_5O$ ($M + H^+$) calcd 1158.4166, found 1158.4175.

3a. ^{1}H NMR and ^{13}C NMR signals show that compound **3a** was a mixture of two isomers: ^{13}C NMR (126 MHz, CS_2/$CDCl_3$) δ 75.17, 74.01, 73.43, 72.97, 72.93, 72.40, 72.22, 71.18, 70.48, 70.10 (only the signal for sp^3 carbons including those for [60]fullerene are listed to indicate the mixture nature); ESI-FT-ICR-HRMS-positive $C_{90}H_{61}N_6$ ($M + H^+$) calcd 1225.4952, found 1225.4958.

Compounds 2b and 3b. To a solution of C_{60} (72 mg, 0.1 mmol) in 10 mL of dichlorobenzene was added 30 equiv of 4-methylpiperidine (0.354 mL, 3.0 mmol). The resulting solution was stirred at rt for 5 days. The reaction was terminated upon confirmation of nearly complete conversion of C_{60} and **1b**. The solution was chromatographed on a silica gel column eluting with petroleum ether to remove dichlorobenzene. Eluting with a petroleum ether/toluene mixture (1:1) gave the first red band as compound **2b** (18 mg, 0.015 mmol, 15%). Eluting with a toluene/ethyl acetate mixture (20:1) gave the second red band as compound **1b** (trace amount) and the third black band as compound **3b** (39 mg, 0.0298 mmol, 30%).

2b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 3.94 (d, 12 Hz, 2H), 3.81−3.68 (m, 8H), 2.81 (t, J = 10.9 Hz, 2H), 2.70−2.67 (m,

dx.doi.org/10.1021/jo5015867 | J. Org. Chem. 2014, 79, 8912−8916

6H), 2.51 (t, J = 10.5 Hz, 2H), 1.86 (d, J = 11.6 Hz, 2H), 1.78−1.75 (m, 8H), 1.45−1.25 (m, 15H), 1.02−0.97 (m, 15H); ^{13}C NMR (126 MHz, CS_2/$CDCl_3$) (all signals represent 2C except as noted) δ 152.84, 152.38, 150.24, 148.74, 148.43, 148.34, 148.05, 148.00, 147.94, 147.75 (1C), 147.35, 147.04 (1C), 146.97, 146.91, 146.51, 145.38, 144.91, 144.21, 144.05, 143.83, 143.68, 143.61, 143.25, 143.01, 142.69, 142.56, 141.53, 140.97, 81.03 (1C), 73.48, 72.96 (1C), 70.78, 53.24, 51.00, 50.87, 50.65, 50.02, 35.76, 35.49, 35.34, 35.28, 35.25, 31.10, 30.98, 30.65 (1C), 22.08, 22.03, 21.94 (1C); ESI-FT-ICR-HRMS-positive $C_{90}H_{62}N_5O$ (M + H$^+$) calcd 1228.4949, found 1228.4970.

Crystals of **2b** suitable for X-ray diffraction were obtained from a mixture of CS_2 and ethanol. Crystal data for $C_{90}H_{61}N_5O$ (M = 1228.44 g/mol): triclinic, space group $P\bar{1}$ (No. 2), a = 14.686(3) Å, b = 14.693(3) Å, c = 19.515(5) Å, α = 80.480(15)°, β = 78.540(14)°, γ = 61.550(12)°, V = 3616.4(15) Å^3, Z = 2, T = 173(2) K, μ (Mo Kα) = 0.067 mm^{-1}, D_{calc} = 1.128 g/cm^3, 26966 reflections measured, 12669 unique reflections (R_{int} = 0.0643), which were used in all calculations. The final R_1 was 0.1172 [$I > 2\sigma(I)$] and wR_2 was 0.3003 (all data). Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC-1010193.

3b. It was difficult to isolate and purify compound **3b**. Additionally, compound **3b** was easy to decompose. Therefore, ^{1}H NMR and ^{13}C NMR data of **3b** were not obtained: ESI-FT-ICR-HRMS-positive $C_{96}H_{73}N_6$ (M + H$^+$) calcd 1309.5891, found 1309.5889.

Compounds 2c and 3c. To a solution of C_{60} (72 mg, 0.1 mmol) in 5 mL of dichlorobenzene was added 90 equiv of 1,2,3,4-tetrahydroisoquinoline (1.126 mL, 9.0 mmol). The resulting solution was stirred at 35 °C for 1 day. The reaction was terminated upon confirmation of nearly complete conversion of C_{60} and **1c**. The solution was chromatographed on a silica gel column eluting with petroleum ether to remove dichlorobenzene. Eluting with a petroleum ether/toluene mixture (1:2) gave the first red band as compound **2c** (49 mg, 0.035 mmol, 35%). Eluting with toluene gave the second red band as compound **1c** (trace amount) and the third black band as compound **3c** (60 mg, 0.0397 mmol, 40%).

2c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15−7.07 (m, 11H), 7.05−6.93 (m, 5H), 6.86 (d, J = 7.5 Hz, 1H), 6.73 (d, J = 7.3 Hz, 2H), 6.51 (d, J = 7.2 Hz, 1H), 4.81 (d, J = 14.6 Hz, 1H), 4.70−4.61 (m, 4H), 4.54−4.49 (m, 2H), 4.41−4.34 (m, 2H), 4.20−4.12 (m, 2H), 3.62−3.49 (m, 8H), 3.25−3.16 (m, 1H), 3.02−2.98 (m, 9H), 2.84 (d, J = 15.9 Hz, 1H); ^{13}C NMR (126 MHz, CS_2/$CDCl_3$) (all signals represent 1C except as noted) δ 153.47, 153.24, 152.52, 151.80, 150.72, 149.25, 148.72, 148.65 (2C), 148.57, 148.46, 148.26 (2C), 148.19 (3C), 148.00, 147.66, 147.56, 147.18 (2C), 147.07 (2C), 147.05 (2C), 146.79, 146.73, 145.48 (2C), 144.92 (2C), 144.54 (2C), 144.27 (2C), 144.16 (3C), 144.08, 143.91, 143.66 (2C), 143.61, 143.40 (2C), 143.04, 142.89, 142.83, 142.74, 142.68, 141.97 (2C), 140.42 (2C), 134.74, 134.67 (2C), 134.65, 134.59, 133.85, 133.77, 133.64, 133.61, 133.56, 132.47, 128.39 (3C), 128.26 (2C), 126.49 (4C), 126.41, 125.93 (3C), 125.73 (3C), 125.54 (3C), 81.61, 73.33, 73.18, 73.01, 70.69, 70.60, 55.15, 53.37, 52.90, 52.75 (2C), 50.26, 47.69 (2C), 47.59, 47.35, 30.37 (2C), 30.23 (3C); ESI-FT-ICR-HRMS-positive $C_{105}H_{52}N_5O$ (M + H$^+$) calcd 1398.4166, found 1398.4208.

3c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30−7.20 (m, 12H), 7.16−6.92 (m, 10H), 6.88 (d, J = 7.4 Hz, 1H), 6.69 (d, J = 7.8 Hz, 1H), 4.84−4.30 (m, 14H), 3.81−3.46 (m, 7H), 3.38−3.30 (m, 1H), 3.18−2.99 (m, 11H), 2.90−2.84 (m, 3H); ^{13}C NMR (126 MHz, CS_2/$CDCl_3$) (all signals represent 1C except as noted) δ 155.11, 154.10, 152.96, 151.55, 150.95 (2C), 150.92, 150.24, 149.94, 149.78, 149.07, 148.77, 148.62, 148.01, 147.94, 147.87, 147.71 (2C), 147.69 (2C), 147.41, 147.35, 147.06, 147.01, 146.97, 146.70, 146.61, 146.44, 146.38, 146.28, 146.12, 145.76, 145.71, 145.60, 145.57, 145.52 (3C), 145.48, 145.24, 145.06, 144.77, 144.58, 144.50, 144.44, 144.29, 143.66, 143.58, 142.70, 142.29, 141.70, 141.14, 140.57, 140.08, 137.11, 134.70, 134.68, 134.65, 134.48, 134.13, 133.63, 133.53, 133.51, 133.42, 133.21, 130.03, 128.49, 128.33, 128.26 (2C), 128.22, 128.09, 126.48, 126.36, 126.31, 126.21 (2C), 126.16, 126.10, 125.93, 125.84, 125.82, 125.74, 125.66, 125.60 (2C), 125.49 (2C), 125.39 (2C), 73.02, 72.35, 71.86 (2C), 70.02, 69.59, 53.34, 53.28, 53.11, 52.91, 52.28, 51.72, 48.07, 47.71, 47.67, 47.47, 46.85, 46.52, 30.18, 30.15, 30.12 (2C), 30.04, 29.94; ESI-FT-ICR-HRMS-positive $C_{114}H_{61}N_6$ (M + H$^+$) calcd 1513.4958, found 1513.5022.

Compounds 2d, 3d, and 4. To a solution of C_{60} (72 mg, 0.1 mmol) in 5 mL of dichlorobenzene was added 120 equiv of *N*-methylbenzylamine (1.545 mL, 12.0 mmol). The resulting solution was stirred at 35 °C for 4 days. The reaction was terminated upon confirmation of nearly complete conversion of C_{60} and **1d**. The solution was chromatographed on a silica gel column eluting with petroleum ether to remove dichlorobenzene. Eluting with a petroleum ether/toluene mixture (3:1) gave the first red band as compound **4** (trace amount) and the second red band as compound **2d** (32 mg, 0.0239 mmol, 24%). Eluting with a petroleum ether/toluene mixture (1:1) gave the third red band as compound **1d** (trace amount). Eluting with toluene gave and the forth black band as compound **3d** (63 mg, 0.0438 mmol, 44%).

2d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.37 (m, 10H), 7.35−7.32 (m, 4H), 7.28−7.21 (m, 8H), 7.16−7.14 (m, 1H), 7.11−7.07 (m, 2H), 5.35 (d, J = 12.9 Hz, 1H), 4.73−4.71 (m, 4H), 4.47 (m, 2H), 4.31 (d, J = 11.1 Hz, 1H), 4.17 (d, J = 12.7 Hz, 1H), 3.71 (d, J = 13.0 Hz, 1H), 2.88 (s, 3H), 2.83 (s, 3H), 2.82 (s, 3H), 2.72 (s, 3H), 2.70 (s, 3H); ^{13}C NMR (126 MHz, CS_2/$CDCl_3$) (all signals represent 1C except as noted) δ 154.14, 153.74, 152.22, 151.81, 150.28, 149.70, 148.85, 148.63 (2C), 148.54 (3C), 148.29, 148.26, 148.17 (2C), 148.10 (2C), 147.93, 147.57, 147.53, 147.21, 147.15, 147.13, 147.04 (2C), 146.75 (2C), 145.36 (2C), 144.89, 144.82, 144.78, 144.72, 144.16, 144.06, 144.03, 143.93, 143.81, 143.70, 143.51 (3C), 143.26, 143.24, 142.96, 142.85, 142.76, 142.71, 142.61, 141.87 (2C), 140.47, 140.16, 138.83 (2C), 138.79, 138.74, 137.77, 128.67 (6C), 128.61 (2C), 128.58 (2C), 128.38 (2C), 128.02 (7C), 127.90 (2C), 127.46, 126.76, 126.68 (2C), 82.44, 73.82, 73.71, 73.31, 71.14, 71.10, 61.28, 59.48, 59.32 (2C), 59.13, 40.42, 38.35, 38.22 (2C), 38.14; ESI-FT-ICR-HRMS-positive $C_{100}H_{52}N_5O$ (M + H$^+$) calcd 1338.4166, found 1338.4166.

3d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.18 (m, 30H), 4.79 (d, J = 13.7 Hz, 1H), 4.64 (d, J = 13.6 Hz, 1H), 4.56−4.50 (m, 2H), 4.46−4.36 (m, 4H), 4.33−4.28 (m, 3H), 3.96 (d, J = 13.6 Hz, 1H), 2.89 (s, 3H), 2.78 (s, 3H), 2.77 (s, 3H), 2.71 (s, 3H), 2.66 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) (all signals represent 1C except as noted) δ 155.93, 153.81, 152.77, 152.08, 151.59, 151.43, 150.21, 150.06, 149.67, 148.99, 148.76, 148.62, 148.12, 147.89 (2C), 147.79 (2C), 147.73 (2C), 147.53, 147.47, 147.10, 147.03, 146.93, 146.77, 146.60 (2C), 146.55, 146.35, 146.14 (2C), 145.83, 145.74, 145.56 (3C), 145.52 (2C), 145.44, 145.18 (2C), 144.86, 144.71, 144.63, 144.42, 144.33, 143.59, 143.52, 142.63, 142.46, 141.75, 141.62, 140.84 (2C), 139.14, 139.09, 138.67, 138.57, 138.07, 136.84, 130.85, 128.69, 128.44 (4C), 128.41 (3C), 128.33 (2C), 128.16 (2C), 128.12 (2C), 128.04 (3C), 127.99 (4C), 127.87 (2C),127.00, 126.93, 126.79, 126.70 (2C), 126.56, 74.00, 73.05, 72.64, 72.29, 70.27, 70.09, 59.57, 59.31, 59.17, 58.17, 58.03, 57.58, 38.81, 38.68, 38.55, 37.82, 37.05, 37.03; ESI-FT-ICR-HRMS-positive $C_{108}H_{61}N_6$ (M + H$^+$) calcd 1441.4952, found 1441.4921.

4: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56−7.53 (m, 4H), 7.37−7.29 (m, 7H), 7.25 (s, 2H), 7.20 (m, 12H), 6.27 (s, 1H), 5.02−4.73 (m, 4H), 4.35−4.18 (m, 4H), 2.93 (s, 3H), 2.81 (s, 3H), 2.80 (s, 6H), 2.60 (s, 3H); ^{13}C NMR (126 MHz, CS_2/$CDCl_3$) (all signals represent 1C except as noted) δ 154.72, 152.62, 152.52, 149.73, 149.19, 148.76, 148.69, 148.64, 148.58, 148.55, 148.27, 148.17, 148.08, 148.00, 147.97, 147.90, 147.87, 147.59, 147.45, 147.31, 147.10, 147.07, 147.00 (2C), 146.97, 146.96, 146.93, 145.80, 145.59, 145.50, 145.42, 145.25, 145.07, 145.04, 145.01, 144.76, 144.68, 144.36, 144.13, 144.00, 143.68, 143.63, 143.29, 143.26, 143.22, 143.19, 143.10, 143.00, 142.68, 142.61, 142.56, 142.31, 140.79, 140.28, 139.18, 139.07, 138.96, 138.56, 135.10, 129.50 (2C), 129.40, 129.02 (2C), 128.79 (2C), 128.71 (2C), 128.55 (2C), 128.10 (2C), 128.07 (2C), 128.04 (2C), 128.03 (2C), 127.94 (2C), 126.99, 126.80, 126.68, 126.65, 97.59 (CH, confirmed by the DEPT spectrum), 93.22, 74.96, 74.61, 73.71, 71.62, 71.16, 61.18, 60.12, 58.49 (2C), 39.68, 38.51, 38.23, 37.98, 33.04; ESI-FT-ICR-HRMS-positive $C_{100}H_{50}N_5O$ (M + H$^+$) calcd 1336.4010, found 1336.3999.

Compound 1d. To a solution of C_{60} (72 mg, 0.1 mmol) in 5 mL of dichlorobenzene was added 30 equiv of *N*-methylbenzylamine (0.386 mL, 3.0 mmol). The resulting solution was stirred at 35 °C for

dx.doi.org/10.1021/jo5015867 | J. Org. Chem. 2014, 79, 8912−8916

4 days. The solution was chromatographed on a silica gel column eluting with petroleum ether to remove dichlorobenzene and unreacted C_{60} (11 mg, 0.015 mmol, 15%). Eluting with a petroleum ether/toluene mixture (1:1) gave the first red band as compound **1d** [46 mg, 0.0378 mmol, 38% (brsm, 45%)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48−7.47 (m, 4H), 7.39−7.38 (m, 4H), 7.32−7.27 (m, 6H), 7.26−7.20 (m, 6H), 4.80 (d, J = 13.5 Hz, 2H), 4.49 (d, J = 13.5 Hz, 2H), 4.42 (d, J = 13.3 Hz, 2H), 4.32 (d, J = 13.3 Hz, 2H), 2.89 (s, 6H), 2.72 (s, 6H); ^{13}C NMR (126 MHz, CS_2/$CDCl_3$) (all signals represent 2C except as noted) δ 151.74, 149.98, 149.29, 149.07, 148.80, 147.53 (1C), 147.46, 147.28, 147.18, 146.89 (4C), 146.74, 146.65, 146.60, 146.01, 145.91, 145.02 (1C), 144.94, 144.58, 144.35, 143.87, 143.68, 143.43, 143.34, 142.94, 142.72, 141.83, 140.04, 138.79, 138.65, 128.43 (4C), 128.35 (4C), 128.14 (4C), 128.07 (4C), 126.88, 126.83, 76.58 (1C), 75.76, 72.16, 71.54 (1C), 59.46, 59.26, 38.97, 38.56; ESI-FT-ICR-HRMS-positive $C_{92}H_{41}N_4O$ (M + H^+) calcd 1217.3275, found 1217.3310.

Compound 2e. To a solution of C_{60} (72 mg, 0.1 mmol) in 10 mL of dichlorobenzene was added 30 equiv of pyrrolidine (0.250 mL, 3.0 mmol). The resulting solution was stirred at room temperature for 2 days. The reaction was terminated upon confirmation of nearly complete conversion of C_{60} and **1e**. The solution was chromatographed on a silica gel column eluting with petroleum ether to remove dichlorobenzene. Eluting with a toluene/ethyl acetate mixture (10:1) gave the first red band as compound **2e** (16 mg, 0.0147 mmol, 15%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 (s, 1H), 3.53 (m, 2H), 3.28−3.27 (m, 12H), 3.09−3.08 (m, 4H), 2.94 (m, 2H), 1.94−1.88 (m, 20H); ^{13}C NMR (126 MHz, CS_2/$CDCl_3$) (all signals represent 2C except as noted) δ 153.05, 152.69, 150.24, 149.08, 148.41, 148.31, 148.06, 148.01, 147.97, 147.76 (1C), 147.45, 146.98 (1C), 146.95, 146.86, 146.70, 145.28, 145.22, 144.09, 143.92, 143.86, 143.82, 143.76, 143.52, 143.28, 142.86, 142.68, 141.86, 140.69, 81.74 (1C), 70.26, 69.74 (1C), 68.18, 52.59, 50.24 (4C), 49.55 (4C), 24.22 (8C), 23.85; ESI-FT-ICR-HRMS-positive $C_{80}H_{42}N_5O$ (M + H^+) calcd 1088.3384, found 1088.3398.

Crystals of **2e** suitable for X-ray diffraction were obtained from a mixture of CS_2 and ethanol. Crystal data for $C_{82}H_{41}ON_5S_4$ (M = 1240.44): triclinic, space group $P\bar{1}$ (No. 2), a = 14.0793(8) Å, b = 14.2340(9) Å, c = 16.9088(10) Å, α = 67.063(6)°, β = 88.451(5)°, γ = 61.280(6)°, V = 2682.4(3) Å^3, Z = 2, T = 179.99(10) K, μ (Mo Kα) = 0.241 mm^{-1}, D_{calc} = 1.536 g/mm^3, 17683 reflections measured, 10504 unique reflections (R_{int} = 0.0353), which were used in all calculations. The final R_1 was 0.0712 [$I > 2\sigma(I)$], and wR_2 was 0.1914 (all data). Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC-1010194.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Selected spectroscopic data for all new compounds and crystallographic data for **2b** and **2e**, including CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: gan@pku.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support was provided by NNSFC (Grants 21272013 and 21132007) and MOST (2011CB808401).

■ REFERENCES

(1) (a) Hirsch, A.; Brettreich, M. *Fullerenes: Chemistry and Reactions*; Wiley-VCH: Weinheim, Germany, 2005. (b) Miller, G. P. *C. R. Chim.* **2006**, *9*, 952.

(2) For example: (a) Maeda-Mamiya, R.; Noiri, E.; Isobe, H.; Nakanishi, W.; Okamoto, K.; Doi, K.; Sugayad, T.; Izumi, T.; Homma, T.; Nakamura, E. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 5339. (b) Nakamura, E.; Isobe, H. *Chem. Rec.* **2010**, *10*, 260. (c) Kornev, A. B.; Khakina, E. A.; Troyanov, S. I.; Kushch, A. A.; Peregudov, A.; Vasilchenko, A.; Deryabin, D. G.; Martynenko, V. M.; Troshin, P. A. *Chem. Commun.* **2012**, *48*, 5461.

(3) (a) Kuwashima, S.; Kubota, M.; Kushida, K.; Ishida, T.; Ohashi, M.; Nogami, T. *Tetrahedron Lett.* **1994**, *35*, 4371. (b) Wang, N. X.; Li, J. S.; Zhu, D. B.; Chan, T. H. *Tetrahedron Lett.* **1995**, *36*, 431. (c) Zhang, X.; Gan, L. B.; Huang, S. H.; Shi, Y. R. *J. Org. Chem.* **2004**, *69*, 5800. (d) Tsuruoka, R.; Nagamachi, T.; Murakami, Y.; Komatsu, M.; Minakata, S. *J. Org. Chem.* **2009**, *74*, 1691. (e) Yang, H.-T.; Liang, X.-C.; Wang, Y.-H.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. *J. Org. Chem.* **2013**, *78*, 11992. (f) Miao, C.-B.; Lu, X.-W.; Wu, P.; Li, J. X.; Ren, W.-L.; Xing, M.-L.; Sun, X.-Q.; Yang, H.-T. *J. Org. Chem.* **2013**, *78*, 12257. (g) He, C.-L.; Liu, R.; Li, D.-D.; Zhu, S.-E.; Wang, G.-W. *Org. Lett.* **2013**, *15*, 1532. (h) Yang, H.-T.; Liang, X.-C.; Wang, Y.-H.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. *Org. Lett.* **2013**, *15*, 4650.

(4) Briggs, J. B.; Montgomery, M.; Silva, L.; Miller, G. P. *Org. Lett.* **2005**, *7*, 5553.

(5) (a) Kampe, K.-D.; Egger, N.; Vogel, M. *Angew. Chem., Int. Ed.* **1993**, *32*, 1174. (b) Sun, Y.-P.; Ma, B.; Bunker, C. E. *J. Phys. Chem. A* **1998**, *102*, 7580. (c) Wang, N. X. *Tetrahedron* **2002**, *58*, 2377. (d) Butts, C. P.; Jazdzyk, M. D. S. *Org. Biomol. Chem.* **2005**, *3*, 1209.

(6) Davey, S. N.; Leigh, D. A.; Moody, A. E.; Tetler, L. W.; Wade, F. A. *J. Chem. Soc., Chem. Commun.* **1994**, 397.

(7) (a) Zhu, B.; Wang, G.-W. *Org. Lett.* **2009**, *11*, 4334. (b) Chuang, S.-C.; Rajeshkumar, V.; Cheng, C.-A.; Deng, J.-C.; Wang, G.-W. *J. Org. Chem.* **2011**, *76*, 1599. (c) Liu, T.-X.; Zhang, Z. B.; Liu, Q. F.; Zhang, P. L.; Jia, P. H.; Zhang, Z. G.; Zhang, G. H. *Org. Lett.* **2014**, *16*, 1020. (d) You, X.; Wang, G.-W. *J. Org. Chem.* **2014**, *79*, 117. (e) Su, Y.-T.; Wang, Y.-L.; Wang, G.-W. *Org. Chem. Front.* **2014**, *1*, 689.

(8) (a) Lawson, G. E.; Kitaygorodskiy, A.; Ma, B.; Bunker, C. E.; Sun, Y.-P. *J. Chem. Soc., Chem. Commun.* **1995**, 2225. (b) Liou, K.-F.; Cheng, C.-H. *Chem. Commun.* **1996**, 1423. (c) Gan, L. B.; Jiang, J. F.; Zhang, W.; Su, Y.; Shi, Y. R.; Huang, C. H.; Pan, J. Q.; Lu, M. J.; Wu, Y. *J. Org. Chem.* **1998**, *63*, 4240. (d) Bernstein, R.; Foote, C. S. *J. Phys. Chem. A* **1999**, *103*, 7244. (e) Nakamura, Y.; Suzuki, M.; O-kawa, K.; Konno, T.; Nishimura, J. *J. Org. Chem.* **2005**, *70*, 8472. (f) Wang, G.-W.; Chen, X. P.; Cheng, X. *Chem.—Eur. J.* **2006**, *12*, 7246. (g) Troshina, O. A.; Troshin, P. A.; Peregudov, A. S.; Lyubovskaya, R. N. *Mendeleev Commun.* **2007**, *17*, 113.

(9) (a) Miyake, Y.; Ashida, Y.; Nakajima, K.; Nishibayashi, Y. *Chem.—Eur. J.* **2014**, *20*, 6120. (b) Lim, S. H.; Yi, J.; Moon, G. M.; Ra, C. S.; Nahm, K.; Cho, D. W.; Kim, K.; Hyung, T. G.; Yoon, U. C.; Lee, G. Y.; Kim, S.; Kim, J.; Mariano, P. S. *J. Org. Chem.* **2014**, *79*, 6946.

(10) Si, W.; Lu, S.; Bao, M.; Asao, N.; Yamamoto, Y.; Jin, T. *Org. Lett.* **2014**, *16*, 620.

(11) (a) Schick, G.; Kampe, K.-D.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2023. (b) Isobe, H.; Ohbayashi, A.; Sawamura, M.; Nakamura, E. *J. Am. Chem. Soc.* **2000**, *122*, 2669. (c) Isobe, H.; Tomita, N.; Nakamura, E. *Org. Lett.* **2000**, *2*, 3663. (d) Isobe, H.; Tanaka, T.; Nakanishi, W.; Lemiègre, L.; Nakamura, E. *J. Org. Chem.* **2005**, *70*, 4826. (e) Lemiègre, L.; Tanaka, T.; Nanao, T.; Isobe, H.; Nakamura, E. *Chem. Lett.* **2007**, *36*, 20. (f) Troshina, O. A.; Troshin, P. A.; Peregudov, A. S.; Kozlovski, V. I.; Lyubovskaya, R. N. *Chem.—Eur. J.* **2006**, *12*, 5569.

(12) Zhang, G.; Hu, X. Q.; Gan, L. B.; Li, Y. L. *Tetrahedron Lett.* **2011**, *52*, 5805.

(13) For an example of related metal free intramolecular oxidative C(sp^3)−O bond formation through C(sp^3)−H functionalization, see: Uyanik, M.; Okamoto, H.; Yasui, T.; Ishihara, K. *Science* **2010**, *328*, 1376.

(14) (a) Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature* **2002**, *419*, 702. (b) Nakamura, E.; Isobe, H. *Acc. Chem. Res.* **2003**, *36*, 807.

(15) See the Supporting Information for a proposed mechanism of the present reactions and discussion about the mechanism.