Synthesis of Pyrrolidine Ring-Fused Fullerene Multicarboxylates by Photoreaction

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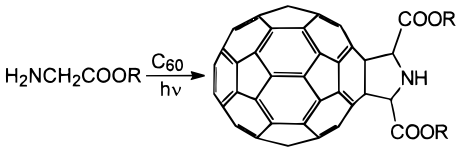
Aminopolycarboxylic esters react with C_{60} under photolysis to produce fullerene multicarboxylates. Irradiation of tetramethyl ethylenediaminetetraacetate (EDTA) with C_{60} yields the EDTA-containing fullerene monoadduct $C_{60}(MeOOCCH)_2NCH_2CH_2N(CH_2COOMe)_2$. In addition, several other C_{60} monoadducts are also isolated and characterized, including compounds due to EDTA fragmentation. Similar results are observed with pentamethyldimethylenetriaminepentaacetate (DTPA). When partially methylated nitrilotriacetic acid is irradiated with C_{60}, decarboxylation occurs and organodihydrofullerene derivatives such as $C_{60}(H)(CH_2N(CH_2COOMe)_2)$ are formed. Radical mechanisms are proposed for both types of photoreactions. The fullerene derivatives are characterized by their spectroscopic data. Photoreactions of C_{60} with other analogous molecules also support the conclusions.

Derivatization of C_{60} has played a key role in the biological studies of fullerenes.[1] The introduction of a suitable pendant group not only improves the solubility of the fullerene but also provides a handle to anchor C_{60} to a specific target for drug delivery and/or photostudy.[2] During the past a few years, water-soluble fullerene derivatives have been reported as HIV protease inhibitors and DNA-cleavage reagents.[3,4] Bioactive lipophilic fullerene steroids have also been prepared that showed inhibition of radiolabeled estradiol binding to the cytosolic estrogen receptor.[5] Several other steroidal fullerenes have also been reported.[6] Despite the wide variety of biological activities reported, much work remains to be done to develop practicable applications for fullerenes.

Fullerene amino acids are of great importance as bioactive reagents. Several methods have been developed for their preparation.[7−10] We have recently reported that glycine esters add directly to C_{60} under photolysis to form pyrrolidine ring-fused fullerenes.[11] Even though multisteps of C−N bond-breaking and formation processes are involved, the photoreaction gave isomerically pure monoadduct very efficiently (80% yield in less than 30 min).



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We have begun to investigate the photoreaction systematically and extended the reaction to aminopolycarboxylates. Aminopolycarboxylic acids such as EDTA and DTPA are among the best known complexones or polydentate ligands.[12] They have been widely used in both fundamental research and practical applications. Their lanthanide complexes are potential immunoassay agents. The Gd complex of DTPA is the first commercial MRI contrast reagent. The attachment of such ligands to C_{60} should open the scope for their potential applications. Here, we report the preparation of EDTA- and DTPA-containing fullerenes. Most of our previous work involves the use of amino acid esters. We have now found serendipitously that amino acids may be decarboxylated and add to C_{60} to form dihydrofullerenes.[13]

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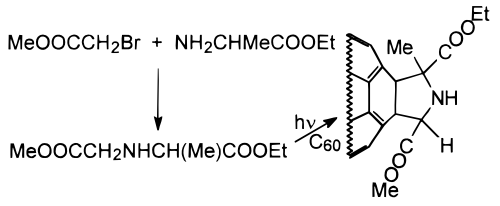
Synthesis of Mono- and Dicarboxylic Fullerene Derivatives

Treatment of L-alanine ester with bromoacetic methyl ester results in the formation of α-methyliminodiacetic ester. Photolysis of the iminodiacetic ester with C_{60} produced compound **2** in high yields. Pure α-alanine ester reacts very slowly with C_{60}. Introduction of the second acetic group to L-alanine improves the photolysis significantly in both the yield of the isomerically pure product and the rate of the reaction.



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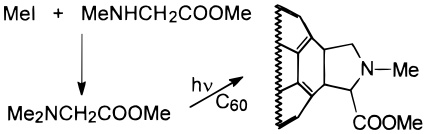
The net result of the reaction is the loss of two hydrogen atoms from the CH_2 and CH carbons, respectively. Unlike the glycine reaction,[11] there is no C−N bond-breaking process involved here. Isolation of the mixed ester derivative **2** strongly supports this conclusion. If there were C−N bond breaking and -formating processes, some other products such as the dimethyl ester anolog of **2** would be produced since the reaction was carried out in a mixture of methanol and toluene.



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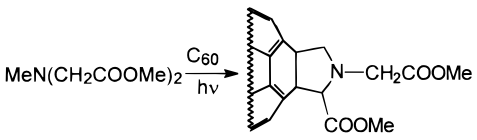
Like the primary and secondary aminocarboxylic acids, tertiary aminocarboxylic acids also react under the same conditions. Sarcosine was first treated with methyl iodide to give the *N*,*N*-dimethylglycine ester. Photolysis of this glycine-derived tertiary aminocarboxylic acid gave **3** as the only isolated product. The net result of the reaction is also a loss of two H atoms, reminiscent of the above iminodiacetic acid reaction. Compound **3** can also be prepared by the 1,3-dipole thermal addition.[11] Thus, heating a mixture of sarcosine and formaldehyde with C_{60} gives a compound with the same ^{1}H NMR and FTIR spectra as those of **3**.



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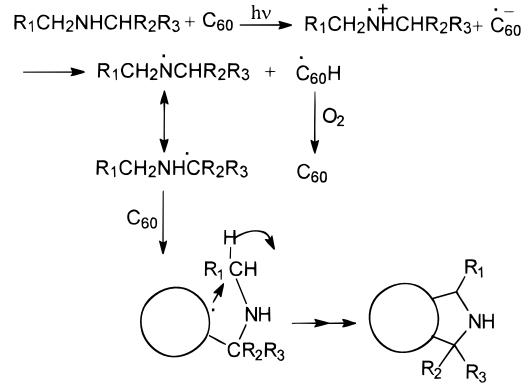
In an extension of the iminodiacetic reaction, the iminodiacetic methyl ester was treated with methyl iodide to yield the *N*-methylnitrilodiacetic ester with two acetic groups attached to the same nitrogen atom. According to the previous results, two products may be expected: one is the symmetric pyrrolidine with the two ester groups attached at the 2,5-positions of the pyrrolidine ring; the other is the unsymmetric product **4**. In the reaction, only the unsymmetric product **4** was isolated. So the methyl group on the N instead of the second methylene group loses the other H atom.

(13) A communication of the decarboxylation work has been published. Zhang, W.; Su, Y.; Gan, L.; Jiang, J.; Huang, C. *Chem. Lett.* **1997**, *10*, 1007.

Scheme 1. Mechanism of Pyrrolidine Ring-fused Fullerene Formation



To confirm its structure, compound **4** was also prepared by the 1,3-dipole thermal addition method, i.e., refluxing a mixture of formaldehyde, iminodiacetic methyl ester, and C_{60}.

To form compound **2**, the initial key step is probably the formation of the α-carbon-centered radical (Scheme 1). The α-carbon-centered radical may be formed by direct H atom transfer. C_{60} is well-known to generate singlet O_2,[14] which may abstract the H from the amino acid. The presence of a small amount of O_2 has been proven to accelerate the photoreaction. Alternatively, the radical may also be formed by electron transfer, followed by proton loss. C_{60} could act as the electron acceptor. The radical then adds to the electron-deficient C_{60}. The cyclization and the formation of the other C−C bond could follow the same procedure. Pathways similar to Scheme 1 can also explain the formation of compounds **3** and **4**.

According to the above-proposed mechanism, the chirality due to the asymmetric carbon of L-alanine part would be changed because of the formation of an sp^2 carbon radical. To confirm the chirality change, we measured the CD spectra of the starting materials and the product. There is no apparent band in the CD spectra of product **2**. A comparison of the spectra indicates that the chirality has indeed been changed.

It is well-known that the α-centered radical is the most stable for amino acids.[15] The combined action of electron-donating amino group and the electron-withdrawing carboxyl group helps to stabilize the radical. Such a "push−pull"-stabilized radical has been extensively studied.[16] Free-radical amino acid reaction is one of the major synthesis methods for amino acid and derivatives.[15]

In a separate study, we found that *β*-alanine ethyl ester does not react with C_{60} under exactly the same photoconditions. This supports the idea that the above α-carbon-centered radical is the reactive species and the α-carbon is the reactive center. If the amino group were the reactive site, *β*-alanine should also add to C_{60}.

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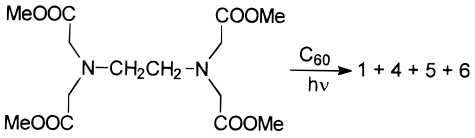
Because of the presence of the two carbon units between the amino and the carbonyl groups in the β-alanine, there is no "push−pull" stabilization effect as in the α-amino acids. Radiolysis results show that amino acids such as β-alanine and ϵ-aminocaproic do not undergo deamination, whereas deamination of α-amino acids through radical mechanism is well documented.[17]

Recently, Sun and co-workers reported that triethylamine adds to C_{60} to form a pyrrolidine ring-fused product under photolysis.[18] Cheng and co-workers later found that irradiation of trimethylamine with C_{60} also yields a pyrrolidine product.[19] For both the two reactions, a two-step photoinduced electron-transfer−proton loss mechanism was proposed.

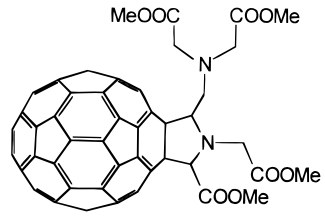
Synthesis of EDTA and DTPA Containing C_{60} Derivatives

The above results have demonstrated that both secondary and tertiary aminocarboxylates can add to C_{60} under photolysis. To explore the photoreaction further, we tried the reaction with the methyl ester of EDTA. EDTA forms stable complexes with almost all metal cations. Such aminoacetic group-containing organic ligands have been named complexones.[12] Formation of a C_{60}−EDTA derivative introduces C_{60} into the complexone family.



Photolysis of the EDTA tetramethyl ester with C_{60} produced four products, namely compounds **1**, **4**, **5** and **6**. The first two were eluted on the silica gel column with toluene. Both of them have been prepared previously using other starting materials. The purity of the EDTA ester was checked by ^{1}H NMR. There is no noticeable impurity. To form the symmetric dicarboxylic compound **1**, the nitrogen ethylene bond N−CH_2CH_2 must be broken in the EDTA molecule; to form the unsymmetric dicarboxylic compound **4**, the ethylene CH_2−CH_2 bond must be broken. The percentage of these two products increases along with the length of the irradiation.

Both compounds **5** and **6** are what we intended. They contain an entire EDTA substituent. The formation of **5** is analogous to the earlier reaction of *N*-methylnitrilodiacetic ester. The ethylene carbon instead of the second methylene carbon next to the carboxyl group is added to C_{60}. Compound **6** is symmetric. Here, two methylene carbons on the same N atom are attached to the 1,2-positions of C_{60}. Between compound **5** and **6**, **5** appears to be the kinetic product, whereas **6** is the thermodynamic product. If the product mixture is chromatographed right after the photolysis, the relative yield of **5** is higher than that of **6**. On the other hand, if the reaction solution is kept at room temperature overnight after the irradiation, the same purification procedure gives **6** in much higher percentage than that of **5**. This indicates that **5** could slowly rearrange into **6** in the



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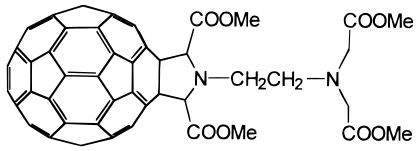

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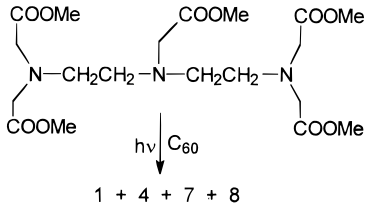
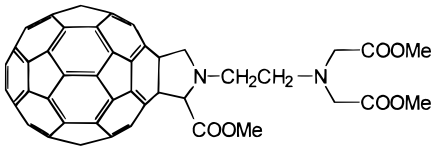
reaction solution. The enhanced thermal stability of **6** over **5** may be due to steric reasons. In compound **6**, the bigger substituent group is further away from the C_{60} sphere.



DTPA is another well-known aminopolycarboxylic acid. It has one more carboxyl group than EDTA. Similar to the EDTA reaction, there are several bands eluted from the silica gel column. Three of them are due to the degradation of DTPA, namely compounds **1**, **4** and **7**. Both **1** and **4** are also produced in the EDTA reaction. Compound **7** is very similar to the EDTA product **6** but has one less ester group. The substituents on compounds **4** and **7** are just the two fragments of a CH_2−CH_2 bond cleavage in a DTPA molecule. The same type of CH_2−CH_2 bond cleavage of a EDTA molecule gives two fragments with the same structure, both of which result in compound **4**.



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From the result of the EDTA reaction, three DTPA-containing products are possible, **8a**−**c**, depending on which two carbons are added to C_{60}. Analogous to the EDTA products **5** and **6**, at least one of the CH groups on the pyrrolidine ring is next to a carboxylic ester group in these three DTPA-containing isomers. The yield of **8a** appears to be the highest and is the only one characterized among them. Compound **8a** is both the kinetic and the thermodynamic product. Unlike the EDTA derivative **5**, it does not rearrange to the sterically favored isomer **8c**. The rearrangement here would require the cleavage of two C−C bonds and the C_{60} sphere to shift a relatively long distance. The two CH groups on the two pyrrolidine rings between **8a** and **8b** are essentially the same. They only slightly differ in the sterical hindrance. The observed preference for **8a** over

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(19) Liou, K. F.; Cheng, C. H. *J. Chem. Soc., Chem. Commun.* **1996**, 1423.

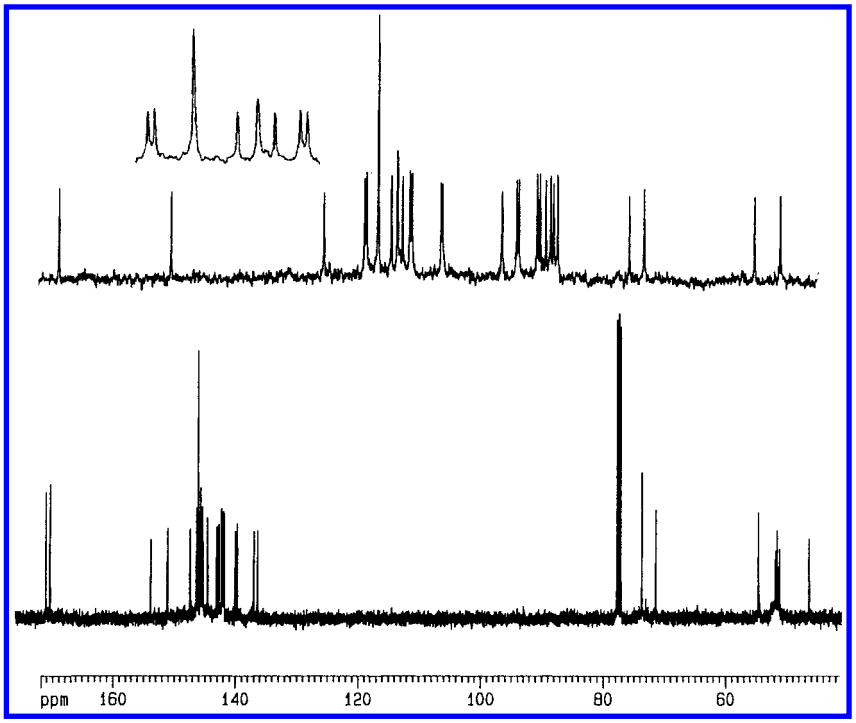
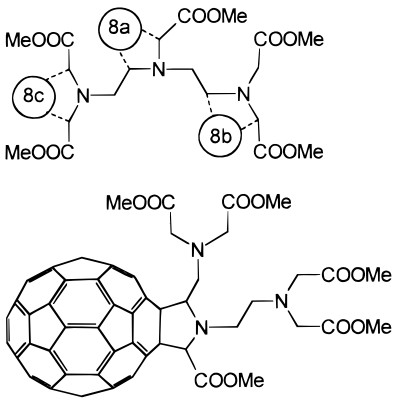


Figure 1. ^{13}C NMR spectrum of **6**.

8b may be due to the slightly stronger electron-donating ability of the center N atom. Thus, a stronger push−pull stabilization effect is present for the α-carbon-centered radical formed from the center acetic group.



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Spectroscopic Data of the EDTA and DTPA C_{60} Derivatives

The compounds were characterized by their spectroscopic data, in particular their ^1H and ^{13}C NMR spectra. All compounds clearly showed bands at around 430 nm on the UV−vis spectra. This band is characteristic of addition at the [6,6] junction. The FDMS showed clearly the molecular ion signal for compounds **5**−**8**.

In the ^1H NMR spectrum of **5**, the methine proton next to the carboxylic group appears as a singlet. The other methine proton on the pyrrolidine ring shows a doublet of doublets due to coupling to the adjacent CH_2 group. The two H atoms of this CH_2 are nonequivalent and appear at 4.20 and 3.53 ppm, respectively, as two doublet of doublets. The other CH_2 group attached to the pyrrolidine also shows germinal coupling. The two methoxy groups distant from the C_{60} are equivalent, so are the two CH_2 groups of the same acetic group, but the two H atoms on each of these two CH_2 are nonequivalent. In the ^1H NMR spectrum, it is evident that a small amount of the stereoisomer is also present. The major stereoisomer may have the transconfiguration. The ^1H NMR spectrum of **6** also shows just one major stereoisomer. The CH_2 group attached to the pyrrolidine exhibits complex multiplets due to germinal coupling and coupling to the adjacent CH_2 group. This indicates that the pyrrolidine probably has a trans geometry. The coupling of the two methylene protons attached to the pyrrolidine should be much simpler in a cis configuration. Such magnetic difference between the cis and transisomers has been successfully used to assign the configuration of heterocyclic bases.[20] In such a photoinduced radical addition reaction, the sterically favored transisomer is expected and has been further proven by ^{13}C NMR spectra.

In the ^{13}C NMR spectrum of **5**, there are a total of 10 sp^3 signals in the range 49−76 ppm, corresponding to the eight types of EDTA ester carbons and the two fullerene carbons at the junction. The carbonyl carbons are in a 1:1:2 intensity ratio at 171.83, 171.42, and 171.14 ppm. For the fullerene sp^2 carbons, 58 signals are observed in the 136−156 ppm range, some of which are overlapped. The ^{13}C NMR spectrum of the symmetric compound **6** (Figure 1) showed fewer signals. There is a total of 30 well-resolved fullerene carbon signals, including the two at the junction. This clearly indicates the above-mentioned trans configuration, which has a C_2 symmetry. For the cis isomer there should be a total of 32 fullerene signals due to the C_s symmetry.

The ^{13}C NMR spectrum of **8a** shows three signals in a 2:2:1 intensity ratio both for the carboxyl carbons and for the methoxy carbons (confirmed by DEPT spectrum). This rules out the structure **8b**, for which there should

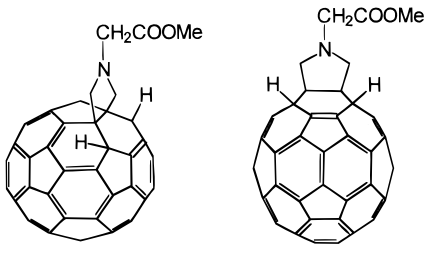
(20) Hill, R. K.; Chan, T. H. *Tetrahedron* **1965**, *21*, 2015.

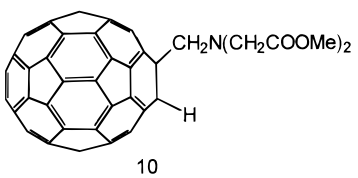
be four methoxy signals. Structure **8c** is ruled out by the number of signals in the fullerene region. There should be 30 fullerene signals for **8c** due to its C_2 symmetry, but 58 signals in the 130−150 ppm region are observed with a few overlapped. The signals show a pattern very similar to that of **5**, in agreement with the similarity between **5** and **8a**.

Preparation of Organodihydrofullerenes by Decarboxylation

The decarboxylation reaction is a case of serendipity. The initial purpose was to investigate the reactivity of nitrilotriacetic ester with C_{60}. Nitrilotriacetic acid has three acetic groups attached to the same N atom. All the previous aminocarboxylic acids have only up to two acetic groups attached to the same N atom. In an attempt to prepare the nitrilotriacetic methyl ester, nitrilotriacetic acid ester was refluxed in methanol under HCl atmosphere. The crude mixture was used directly without further purification except the pH of the solution was adjusted to around 8.5 by addition of sodium carbonate. Its photoreaction with C_{60} was repeated several times. Each time some compound **1** could be isolated. It appears that **1** is probably the most stable product in this system. Several reactions give it as a degradation byproduct, such as those of EDTA and DTPA.

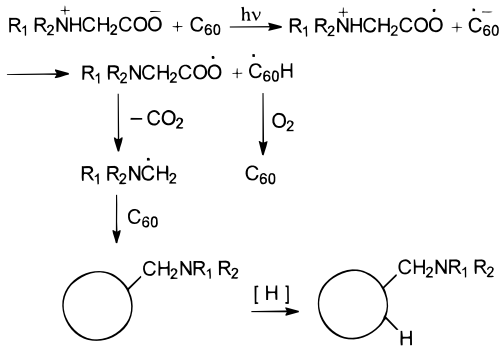
Two other products were also isolated from the above reaction, namely compounds **9** and **10**. There are two structures possible for compound **9**. Structure **9A** is the bis-[6,6] closed adduct, reminiscent of the 1,2,3,4-tetrahydrofullerene $C_{60}H_4$.[21b] Structre **9B** is the bis-[6,5] closed C_{60} adduct. Wilson et al. reported a similar tetrahydro fullerene adduct in the irradiation of 1,3-diones with C_{60}.[21a] Both **9A** and **9B** have a pyrrolidine ring and two H atoms on the same six-membered ring. The NMR data could not distinguish them since they both have a C_s symmetry. A plausible explanation for its formation is that some monoesterified product $MeOOCCH_2N(CH_2COOH)_2$ is present in the crude mixture of the esterification reaction. To form compound **10**, some bisesterified product $(MeOOCCH_2)_2NCH_2COOH$ is probably present. It has been shown that acids are easier to decarboxylate than the corresponding ester. In the 1,3-dipole addition reactions of sarcosine with C_{60}, CO_2 is lost, whereas in the reaction of sarcosine esters with C_{60}, the ester group remains on the pyrrolidine.[22]





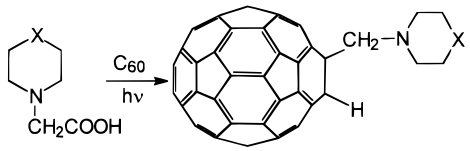
To test the assumption of the presence of monoesterified product, iminodiacetic acid was refluxed with chloroacetic methyl ester in methanol at pH 9. The resulting mixture was then irradiated with C_{60}. Indeed, compound **9** was isolated as the major product. Another side product isolated here is again compound **1**. To test the assumption of the presence of bisesterified product, iminodiacetic methyl ester was refluxed with bromoacetic acid in methanol at pH 9. The resulting mixture yielded compound **10** when irradiated with C_{60}.

Scheme 2. Mechamism of Dihydrofullerene Formation



The reaction between iminodiacetic acid and chloroacetic methyl ester was repeated under different conditions. If the reaction was stopped after refluxing for 4 h, irradiation of the mixture with C_{60} gave just **9** and **1**. When the refluxing was continued for 12 h, irradiation of the mixture with C_{60} gave a third product, **10**. There are two carbonyl ester groups in compound **10**. So in the slightly basic methanol solution, the acetic acid groups could be esterified by refluxing, and some nitrilotriacetic monoester was converted to the bisester.

To further verify the decarboxylation of nitrilotriacetic acid, we prepared the following acetic acid derivatives and investigated their photoreaction with C_{60}. As expected, decarboxylation takes place, and products **11** and **12** were isolated.



X = CH_2, 11; O, 12

A possible path way is shown in Scheme 2. Similar to the ester reaction pathway, the first step is the electron transfer and proton loss. Under the conditions employed here, these steps are easily initiated. The CO_2 loss from carboxyl radicals is well-known.[23] The so-formed aminomethyl radical then adds to C_{60}. The final step is the abstraction of hydrogen from the environment. The alkylation of electron-deficient molecules by decarboxylation via photoinduced electron transfer is also well-

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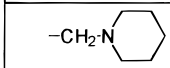
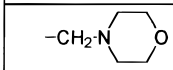
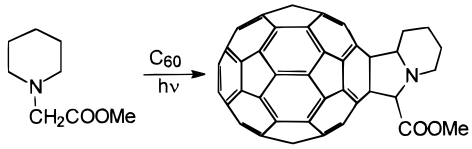
Table 1. Fullerenyl Proton Chemical Shifts of Selected Dihydrofullerenes with the General Formular C_{60}(H)R

Compounds (R)	Chemical Shift (δ)	Ref.
-H	5.93	25
-Me	6.04	26
-Et	6.45	26
$-CHNMe_2$	7.04	18
$—C\equiv C—SiMe_3$	6.92	27
	6.95	
	6.97	
$-CH_2N(CH_2COOMe)_2$	7.11	
9	6.03	

known.[24] These reactions usually give many byproducts, and the yields of alkyldihydro derivatives are less than 20%.

Photolysis of the methyl ester of the piperidineacetic acid still follows the previous pattern, yielding the pyrrolidine ring-fused derivative **13**.



13

Characterization of Organodihydrofullerenes

All the NMR data were obtained using a mixture of CS_2 and $CDCl_3$ in a 10:1 ratio as the solvent except for compound **9**, for which an additional sample was prepared using *o*-dichlorobenzene-d_4 as the solvent. All the ^{1}H NMR spectra showed a clear fullerenyl proton. Table 1 shows a comparison of the chemical shifts between several dihydrofullerenes in the literature and the derivatives prepared here. It has been well demonstrated that the chemical shift of the fullerenyl proton depends on the steric size of the adjacent group. The increased size of the adjacent group causes downfield shift. For example, the chemical shift changes from 6.04 to 6.67 ppm on going from C_{60}(H)Me to C_{60}(H)-*t*-Bu.[26] Our compounds also support this trend. Among compounds *11*, *12*, and *10*, the steric hindrance of the R group increases from the six-membered ring to the noncyclic iminodiacetic group. In correspondence with this order, the chemical shifts of the fullerenyl proton also increase from 6.9 to 7.1 ppm. Between the two sterically comparable compounds **11** and **12**, the chemical shifts are virtually the same.

Compound **9** exhibits fullerenyl proton at 6.03 ppm (Figure 2). This chemical shift is only slightly greater than that of the dihydrofullerene and close to that of C_{60}(H)Me with the smallest R group methyl. This strongly suggests that the structure of **9** is different from the 1,2-addition. The two protons on each methylene group of the pyrrolidine ring are nonequivalent. They appear at 4.07 and 4.49 ppm as two doublets with a germinal coupling constant of 9.2 Hz. The CH_2 next to the ester group appears as a singlet, reflecting the mirror plane bisecting the pyrrolidine ring.

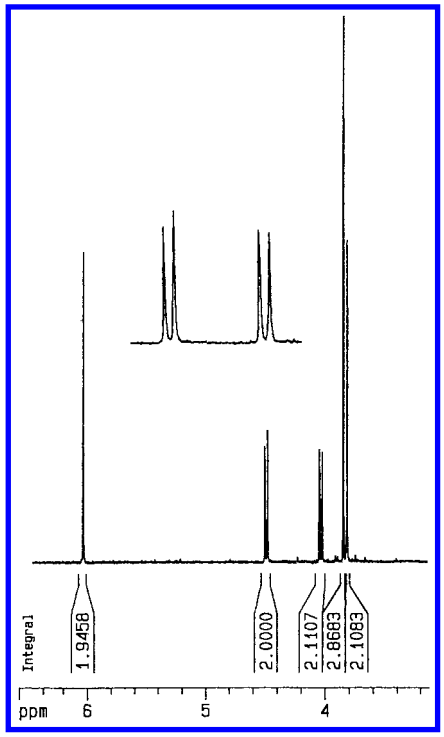


Figure 2. ^{1}H NMR spectrum of **9**.

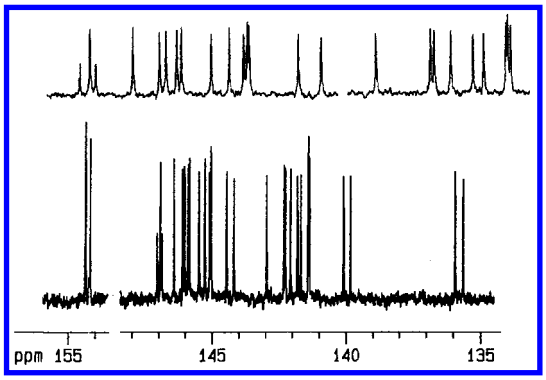


Figure 3. ^{13}C NMR spectrum of **10**.

The ^{13}C NMR spectrum confirms the proposed structure. The spectrum of **10** (Figure 3) shows a distinct signal at 57.36 ppm for the fullerenyl C−H. The assignment was carried out by performing a DEPT spectrum. Unlike the spectrum of **6**, there are 32 well-resolved fullerene carbon signals, reflecting the C_s symmetry. The four fullerene carbons located on the mirror plane are with half-intensity compared to others. Compounds **11** and **12**, also with C_s symmetry, show an almost identical pattern on the ^{13}C NMR spectra. The solubility of **9** is smaller. The signals from saturated CS_2 and $CDCl_3$ were not intense enough to assign all the signals. When the solvent was changed to *o*-dichlorobenzene-d_4, all the signals appeared as expected. The DEPT spectrum located the CH_3, CH, and two CH_2 signals at 51.25, 56.28, 53.79, and 72.05 ppm, respectively. The carbonyl ester carbons appear at 169.13 ppm. In the 140−151 ppm

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(25) Henderson, C. C.; Cahill, P. A. *Science* **1993**, *259*, 1885.
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region, there are 30 signals corresponding to the remaining 56 fullerene sp^2 carbons.

Summary

Photolysis of aminopolycarboxylates with C_{60} has been shown to be an effective method for the preparation of isomerically pure fullerene derivatives. Both aminocarboxylic acids and aminocarboxylic esters are reactive toward C_{60} under the photochemical conditions. For the acids, decarboxylation occurs and organodihydrofullerenes are formed; for the esters, pyrrolidine ring-fused fullerenes are the major products. All the reactions involve radical formation. Unlike the primary amino acid esters that undergo complicated bond-breaking and -forming processes, amino acid esters with secondary and tertiary amino groups can add to C_{60} by simply losing two H atoms. Compared to the well-known 1,3-dipole addition method for the preparation of pyrrolidine ring-fused fullerenes, the photoreaction reported here avoids the use of aldehydes or ketones and is specially suited for the fullerene-containing complexones such as the EDTA C_{60} derivative.

Experimental Section

General Methods. Reagents were all reagent-grade commercials. C_{60} includes traces of solvents. EDTA tetramethyl ester was prepared according to the literature.[28] DTPA pentamethyl ester was prepared in a similar way. All the reactions were carried out under atmosphere without any special caution to exclude air. All the photochemical reactions were carried out similarly. Various household light bulbs can be used as the light source. In this experiment, an overhead project light bulb (250 W) was used for most of the reactions, which was cooled by a water jacket and emerged into the reaction container.

Compound 2. L-alanine ethyl ester and bromoacetic methyl ester in 1:1.4 ratio were mixed in methanol. The pH of the solution was adjusted with sodium carbonate to around 8.5. The solution was refluxed for 8 h and then filtered. During the refluxing, sodium carbonate was added occasionally to maintain the pH at 8.5. Enough of the methanol filtrate (about 30 mL) was added to a C_{60} (60 mg) toluene (200 mL) solution so that the ratio between C_{60} and the ester is about 1:100. To make the solution homogeneous, some toluene should be added if the C_{60} was precipitated by methanol; some methanol should be added if the solution separated into two layers. The resulting solution was irradiated until the color changed from purple to reddish (about 30 min). Solvent was removed in a vacuum and the residue chromatographed over a silica gel column using toluene as eluent. Toluene first eluted unreacted C_{60} (10 mg) and then compound **2** as well separated bands. The yield is about 50% on the basis of converted C_{60}. Crystalline solid was obtained upon slow evaporation of a CS_2/petroleum ether solution. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ: 5.69 (s, 1H), 4.42 (m, 1H), 4.25 (m, 1H), 3.88 (s, 3H), 2.40 (s, 3H), 1.25 (t, 3H). ^{13}C NMR (100.6 MHz, CS_2/$CDCl_3$) δ: 171.34 (*C*OO), 169.56 (*C*OO), 153.01, 151.65, 150.94, 150.19, 147.11, 147.09, 146.35, 146.33, 146.31, 146.27, 146.25, 146.00, 145.98, 145.95, 145.75, 145.73, 145.65, 145.61, 145.39, 145.37, 145.36, 145.33, 145.31, 145.24, 145.22, 145.18, 144.87, 144.36, 144.34, 144.26, 144.24, 143.16, 143.11, 143.08, 142.74, 142.71, 142.69, 142.37, 142.33, 142.28, 142.19, 142.10, 142.04, 142.01, 141.76, 141.74, 141.71, 141.57, 139.80, 139.79, 139.75, 139.15, 136.34, 136.32, 136.25, 136.23, 136.07, 136.04, 77.06, 76.83, 80.88, 72.53, 62.62, 52.95, 25.33, 14.11. FDMS *m*/*z*: 893 (M^+ − 15 + 1). UV−vis ($CHCl_3$): 258, 313, 428 nm. Anal. Calcd for $C_{68}H_{13}NO_4$: C, 89.96; H, 1.44; N, 1.54. Found: C, 89.28; H, 1.22; N, 1.23.

Compound 4 was prepared using the same procedure as that for compound **2**. The yield is about 60% on the basis of converted C_{60} (about 20% could be recovered). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ: 5.60 (s, 1H), 4.77−5.06 (q, 2H), 4.22 (q, 2H), 3.90 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (100.6 MHz, CS_2/$CDCl_3$) δ: 169.24 (*C*OOCH$_3$), 168.60 (*C*OOCH$_3$), 154.28 (2C), 153.46, 152.58, 151.83, 150.43, 147.01, 146.90, 146.13, 146.04, 145.94 (3C), 145.70 (4C), 145.44, 145.42, 145.32, 145.25, 145.18 (2C), 145.10 (2C), 145.07, 144.90 (3C), 144.34, 144.13 (2C), 144.05, 142.72 (3C), 142.35, 142.31 (3C), 141.86 (3C), 141.75, 141.70, 141.59, 141.49 (2C), 141.46, 141.43, 139.99, 139.94, 139.38, 139.26, 137.47, 136.12, 135.90, 135.39, 73.80, 72.19, 68.66, 64.22, 51.56, 51.19, 50.48. FT-IR: 527, 1173, 1188, 1202, 1431, 1738, 1751 cm^{-1}. FDMS *m*/*z*: 895 (M^+ + 1), 837 (M^+ − Me). UV−vis ($CHCl_3$): 256, 310, 430 nm. Anal. Calcd for $C_{67}H_{11}O_4N$: C, 90.03; H, 1.24; N, 1.57. Found: C, 89.60; H, 0.95; N, 1.30.

Photolysis of EDTA Tetramethyl Ester with C_{60}. To a C_{60} (60 mg, 0.08 mmol) solution in 250 mL of toluene was added 0.7 g (2.0 mmol) of EDTA tetramethyl ester in 10 mL of methanol. The mixture was irradiated until the color changed from purple to slightly reddish (about 30 min). The solvent was removed by a rotavapor. The residue was chromatographed on silica gel. Toluene first eluted 10 mg of unreacted C_{60} and then compound **4** (6 mg, 0.0067 mmol) in 10% yield based on converted C_{60}. The third band was compound **1** (6 mg, 0.0067 mmol), also in 10% yield on the basis of converted C_{60}. At this stage, the eluting solvent was changed to toluene/ethyl acetate 4:1. Compounds **5** and **6** were eluted as two well- separated bands. The yields of **5** and **6** were about the same at 25% on the basis of converted C_{60} (19 mg, 0.017 mmol).

Compound 5. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ: 5.82 (s, 1H), 5.60 (q, 1H), 5.04 (d, 1H), 4.20 (q, 1H), 4.18 (d, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.85 (d, 2H), 3.75 (d, 2H), 3.71 (s, 6H), 3.53 (q, 1H). ^{13}C NMR (100.6 MHz, CS_2/$CDCl_3$) δ: 171.83 (1C, *C*OOCH$_3$), 171.42 (1C, *C*OOCH$_3$), 171.14 (2C, 2*C*OOCH$_3$), 155.06, 153.89, 152.40, 150.91, 147.37, 147.36, 147.31, 146.64, 146.61, 146.45, 146.37, 146.35 (2C), 146.26, 146.19, 146.17, 146.15, 146.09, 146.05, 145.99, 145.72, 145.52 (2C), 145.45 (2C), 145.38, 145.36, 145.34, 145.33, 145.28, 145.24 (2C), 145.22, 143.15, 143.02, 142.74, 142.66 (2C), 142.64, 142.24 (2C), 142.13 (3C), 142.04, 142.01, 141.88, 141.84, 141.72, 141.67, 140.25, 139.88, 139.67, 139.34, 137.01, 136.99, 136.38, 136.01, 75.12, 73.12, 71.75, 66.84, 56.82, 54.68 (2C), 52.00, 51.95, 51.64 (2C), 49.94. FT-IR: 527, 1017, 1174, 1203, 1351, 1433, 1740 cm^{-1}. FDMS *m*/*z* 1066 (M^+). UV−vis ($CHCl_3$): 256, 311, 431 nm.

Compound 6. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ: 6.07 (s, 2H), 3.90 (d, 2H), 3.81 (s, 6H), 3.78 (d, 2H), 3.70 (s, 6H), 3.47−3.50 (m, 2H), 3.18−3.32 (m, 2H). ^{13}C NMR (100.6 MHz, CS_2/$CDCl_3$) δ: 170.97 (2C, 2*C*OOCH$_3$), 170.28 (2C, 2*C*OOCH$_3$), 153.83, 151.12, 147.42, 146.42, 146.38, 146.10 (6C), 145.79, 145.64 (4C), 145.52, 145.34, 145.30, 144.60, 144.56, 143.12, 142.77, 142.71, 142.27, 142.20, 142.07, 141.95, 141.88, 141.78, 140.06, 139.70, 137.02, 136.40 (all represent 2C except indicated), 73.71 (2C, *C*HCOOCH$_3$), 71.46 (2C, sp^3 C_{60}), 54.59 (2C, 2*C*H$_2$COOCH$_3$), 51.79 (2C, 2COO*C*H$_3$), 51.56 (1C, *C*H$_2$CH$_2$), 51.18 (2C, 2COO*C*H$_3$), 46.35 (1C, CH$_2$*C*H$_2$). DEPT spectrum located the H containing carbons. FT-IR: 527, 1015, 1100, 1175, 1204, 1247, 1346, 1433, 1664, 1747 cm^{-1}. FDMS *m*/*z*: 1066 (M^+). UV−vis ($CHCl_3$): 256, 312, 429 nm. Anal. Calcd for $C_{74}H_{22}O_8N_2 \cdot 3H_2O$: C, 79.00; H, 2.47; N, 2.56. Found: C, 79.28; H, 2.52; N, 2.50.

Photolysis of DTPA tetramethyl ester with C_{60} was carried out using the same procedure as that for the EDTA analogue. Recovery of C_{60} was ~10%. The yields of compounds **7** and **8** are around 5% and 10% on the basis of converted C_{60}.

Compound 7. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ: 5.18 (d, 1H), 5.12 (s, 1H), 4.31 (d, 1H), 3.77 (s, 3H), 3.76 (s, 4H), 3.61 (s, 6H), 3.44 (m, 1H), 3.30 (m, 1H), 3.22 (m, 1H), 3.09 (m, 1H).

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^{13}C NMR (100.6 MHz, CS_2/$CDCl_3$) δ: 76.70 (1C, *C*HCOOCH$_3$), 64.92 (1C, CH_2N), 54.52 (2C, 2*C*H$_2$COOCH$_3$), 51.58 (1C, $-CH_2-$), 51.30 (1C, COO*C*H$_3$), 50.74 (2C, 2COO*C*H$_3$), 50.50 (1C, $-CH_2-$). DEPT spectrum located the H containing carbons. FDMS *m*/*z*: 1008 ($M^+ + 1$).

Compound 8a. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ: 5.78 (s, 1H), 5.53 (t, 1H), 4.83 (b, 1H), 4.74 (b, 1H), 4.00 (m, 2H), 3.84 (s, 3H), 3.79 (m, 4H), 3.75 (m, 4H), 3.72 (s, 6H), 3.66 (s, 6H), 3.31 (m, 2H). ^{13}C NMR (100.6 MHz, CS_2/$CDCl_3$) δ: 171.48 (2C, 2COOCH$_3$), 171.23 (1C, COOCH$_3$), 170.93 (2C, 2*C*OOCH$_3$), 155.60, 153.79, 152.47, 151.31, 147.25, 147.18, 146.99, 146.73, 146.30 (2C), 146.27, 146.22, 146.19, 146.07, 145.99 (2C), 145.93, 145.62, 145.50, 145.41, 145.35 (2C), 145.28, 145.24 (3C), 145.12, 144.60, 144.57, 144.46, 144.27, 143.09, 142.97, 142.69, 142.64 (2C), 142.59, 142.24, 142.18, 142.16, 142.12, 142.06, 142.00, 141.93, 141.85 (2C), 141.79, 141.69, 141.67 (2C), 140.19, 139.65, 139.62, 139.12, 136.84, 136.56, 136.12, 135.72, 74.80 (1C, C*H*COOCH$_3$), 73.74 (1C, sp^{3}C$_{60}$), 72.15 (1C, sp ^{3}C$_{60}$), 68.41 (1C, $-CH-$), 55.95 (1C, $-CH_2-$), 55.13 (2C, 2C*H*$_2$COOCH$_3$), 54.47 (2C, 2C*H*$_2$COOCH$_3$), 53.39 (1C, $-CH_2-$), 51.42 (1C, COOCH$_3$), 51.38 (2C, 2COOCH$_3$), 51.28 (2C, 2COOCH$_3$), 46.83 (1C, $-CH_2-$). DEPT spectrum located the H containing carbons. FT-IR: 527, 1015, 1170, 1203, 1265, 1350, 1402, 1433, 1711, 1739 cm^{-1}. FDMS *m*/*z*: 1082 (M^+). UV−vis ($CHCl_3$): 255, 310, 431 nm. Anal. Calcd for $C_{79}H_{31}O_{10}N_3$·2.5H_2O: C, 77.12; H, 2.88; N, 3.43. Found: C, 77.32; H, 2.96; N, 3.4.

Preparation of Compounds 9 and 10. To an iminodiacetic acid solution (5.32 g, 40 mmol) in 250 mL of methanol were added 8.48 g (80 mmol) of anhydrous sodium carbonate and 8.68 g (80 mmol) methyl chloroacetate. The mixture was stirred at room temperature for 12 h and then refluxed for another 12 h. The pH of the solution was adjusted with sodium carbonate to 8.5 and then filtered. One-eighth of the filtrate was taken and diluted with methanol to 50 mL. This solution containing about 5 mmol of nitrilotriacetate was added to a C_{60} (72 mg, 0.1 mmol) solution in 250 mL of toluene. To make the solution homogeneous, more methanol was added (about 30−50 mL). The reaction flask was fitted with a condenser. The mixture was irradiated for 2.5 h with two 150 W high-pressure fluorescent bulbs (the same as the bulbs on the street in Beijing). During the photolysis, the solution began to reflux after 1 h. The solution was treated with water twice (20 mL each time) to separate some water-soluble components. The organic solvents were evaporated. The residue was chromotographed on silica gel using toluene as eluent. Unreacted C_{60} (40 mg, 0.055 mmol) and compounds **9** (15 mg, 0.018 mmol), **10** (6.7 mg, 0.007 mmol), and **1** (6 mg, 0.007 mmol) were eluted as well-separated bands.

Compound 9. ^{1}H NMR (400 MH$_Z$, $CDCl_3$/CS_2) δ: 3.80 (s, 2H), 3.84 (s, 3H), 4.04 (d, 2H), 4.47 (d, 2H), 6.03 (s, 2H). ^{13}C NMR (100.6 MH$_Z$, *o*-$C_6D_4Cl_2$/CS_2) δ: 169.13 (COOMe), 150.36, 150.28 (1C), 149.51, 149.30, 149.18 (1C), 149.16, 148.72, 148.23, 146.99, 146.57, 146.42, 145.65, 145.18, 145.12, 144.79, 144.63, 144.39, 144.18, 144.14, 143.73, 143.00, 142.85 (4C), 142.70(1C), 142.37, 142.30 (1C), 141.78, 141.22, 136.24, 135.19 (all represent 2C except indicated), 72.05 (2CH$_2$), 61.74 (sp^3 2C), 56.28 (2CH), 53.79 (CH_2), 51.25 (CH_3). DEPT spectrum located the H-containing cabons. FT-IR: 522, 530, 558, 567, 581, 1020, 1125, 1165, 1187, 1201, 1266, 1420, 1429, 1462, 1748 cm^{-1}. FDMS (*m*/*z*, relative intensity): 837 (M^+, 100), 720 (C_{60}, 18). UV−vis ($CHCl_3$): 257, 433 nm.

Compound 10. ^{1}H NMR (400 MHz, $CDCl_3$/CS_2) δ: 3.76 (s, 6H), 4.15 (s, 4H), 4.72 (s, 2H), 7.11 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$/CS_2) δ: 170.16 (2COOMe), 154.36, 154.19, 147.07 (1C), 146.95, 146.88 (1C), 146.44, 146.12, 146.04, 145.91, 145.86, 145.50, 145.28, 145.11, 145.07, 145.05, 144.46, 144.18, 142.96, 142.31, 142.27, 142.07, 141.81, 141.68, 141.42, 141.40, 141.36, 140.08, 139.84, 135.92, 135.63 (all signals represent 2C except indicated). 68.13 (CH), 67.10, 57.35 (CH_2), 56.09 (CH_3), 51.17 (CH_2). DEPT spectrum located the H containing carbons. FT-IR: 527, 574, 998, 1012, 1144, 1169, 1203, 1261, 1384, 1411, 1429, 1742 cm^{-1}. FDMS *m*/*z*: 895 ($M^+ + 1$). UV−vis ($CHCl_3$): 257 (with shoulder centered at 328), 434 nm. Anal. Calcd for $C_{67}H_{13}O_4N$: C, 89.83; H, 1.46; N, 1.56. Found: C, 90.20; H, 1.30; N, 1.38.

Compound 11. Piperidinoacetic acid (715 mg, 5.0 mmol) in 50 mL of methanol (pH around 8.5) was added to a solution of C_{60} (72 mg, 0.10 mmol) in toluene (200 mL). The resulting mixture was irradiated under stirring for 10 min. The solvent was removed. Isolation by flash column chromatography on silica gel using toluene as eluent afforded 25 mg of unreacted C_{60} and compound **11** (37 mg, in 70% yield based on converted C_{60}). ^{1}H NMR (400 MHz, $CDCl_3$/CS_2) δ: 1.71 (m, 2H), 1.93 (m, 4H), 3.23 (m, 4H), 4.33 (s, 2H), 6.95 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$/CS_2) δ: 155.53, 154.66, 147.41 (1C), 147.33, 147.28 (1C), 146.85, 146.43, 146.26, 146.21, 145.88, 145.55, 145.46, 145.44, 144.78, 144.63, 143.35, 143.16 (4C), 142.66, 142.65, 142.44, 142.14, 142.08, 141.95, 141.75, 141.72, 140.40, 140.22, 136.30, 135.99, 72.59, 67.36, 58.37, 57.04 (2C), 30.29, 27.39, 24.97. FT-IR: 512, 527, 574, 1114, 1161, 1182, 1427, 1437, 1462, 1511 cm^{-1}. UV−vis ($CHCl_3$): 258, 324, 431 nm. Anal. Calcd for C_{60}H[$CH_2N(CH_2)_5$]0.5H_2O: C, 95.87; H, 2.02; N, 1.67. Found: C, 95.64; H, 1.70; N, 1.69.

Compound 12 was prepared using the same procedure as that for compound **11**. The yield is about 60% on the basis of converted C_{60} (about 10% could be recovered). ^{1}H NMR (400 MHz, $CDCl_3$/CS_2) δ: 3.28 (t, 4H), 3.99 (t, 4H), 4.38 (s, 2H), 6.97 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$/CS_2) δ: 155.04, 154.36, 147.48, 147.32, 147.23, 146.28, 146.49, 146.47, 146.32, 146.27, 145.85, 145.63, 145.51, 145.50, 145.48, 144.82, 144.61, 143.38, 142.72, 142.69, 142.41, 142.17, 142.08, 141.88, 141.80, 141.76, 140.49, 140.28, 136.17, 136.09, 72.21 (CH_2), 67.46 (2CH_2), 66.85 (sp^3 C), 58.26 (CH), 55.98 (2CH_2). DEPT spectrum located the H containing carbons. FDMS *m*/*z*: 822 (M^+). UV−vis ($CHCl_3$): 258, 327, 434 nm.

Compound 13 was prepared using the same procedure as that for **2**. The yield is about 70% on the basis of converted C_{60} (about 10% could be recovered). ^{1}H NMR (400 MHz, $CDCl_3$/CS_2) δ: 1.75 (m, 1H), 2.01 (m, 3H), 2.25 (m, 1H), 2.67 (m, 1H), 3.01 (m, 1H), 3.54 (m, 1H), 3.88 (s, 3H), 5.07 (q, 1H), 5.48 (s, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$/CS_2) δ: 170.01, (COOMe), 155.51, 154.11, 154.04, 150.44, 147.38, 147.26, 146.76, 146.66, 146.35 (2C), 146.32, 146.30, 146.20, 146.09, 146.08, 145.99 (2C), 145.71, 145.55, 145.54, 145.53, 145.42, 145.34 (2C), 145.31, 145.28, 145.15, 144.74, 144.65, 144.55, 144.34, 144.20, 143.13, 143.11 (2C), 143.05, 142.74, 142.70 (2C), 142.60, 142.36, 142.24, 142.23, 142.21, 142.10, 142.08, 142.06, 141.95, 141.84 (2C), 141.77, 141.72, 140.31, 140.20, 139.95, 139.66, 137.90, 136.48, 136.34, 76.17, 74.35, 71.48, 69.23, 51.21, 48.76, 31.57, 26.25, 24.91. FDMS *m*/*z*: 875 (M^+). UV−vis ($CHCl_3$): 256, 309, 430 nm. Anal. Calcd for C_{60}[$CH(CH_2)_4NCHCOOCH_3$]: C, 92.81; H, 1.25; N, 1.33. Found: C, 93.25; H, 1.50; N, 1.60.

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Supporting Information Available: Characterization data and ^{1}H and ^{13}C NMR and FDMS data for **5**, **6**, **8**−**10**, and **12** (26 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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