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Novel Reactions of [60]Fullerene with Amino Acid Esters and Carbon Disulfide

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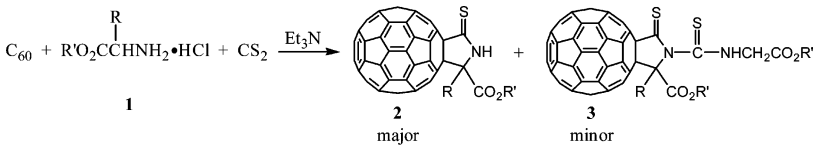

Novel reactions of C_{60} with amino acid ester hydrochlorides and CS_2 in the presence of Et_3N affording fullerene derivatives **2** and **3** containing biologically active amino acids, thioamide, and thiourea units have been investigated. The thioamide groups in compounds **2** are sensitive to moisture and can easily be hydrolyzed to amide groups.

Introduction

A large variety of sulfur-containing [60]fullerene (C_{60}) derivatives have been made due to their interesting optoelectronic properties.[1] Fullerene dyads and triads such as C_{60}-oligothiophene/polythiophene,[2] C_{60}-oligothiophene-C_{60}[3] and C_{60}-tetrathiofulvalene/π-extended tetrathiofulvalene,[4] and C_{60}-tetrathiofulvalene/π-extended tetrathiofulvalene-C_{60}[4j,5] have been intensively investigated. Many reactants involving sulfur atom as reacting species in fullerene reactions have been reported. The main types of sulfur reagents for fullerene functionalization are sulfones[2b,6] and sultines,[7] which have been utilized to prepare C_{60}-porphyrin hybrids,[6d,g] C_{60}-chlorin dyad,[6e] and C_{60}-ZnP rotaxane.[6i] Other reported sulfur reagents in fullerene chemistry are stabilized sulfonium ylides,[8] α,β-unsaturated thiocarbonyl compound,[9] *o*-thioquinone methide,[10] thiocarbonyl ylide,[11] heterocyclic masked 1,3-dipoles 5-imino-1,2,4-thiadiaolidine-3-ones,[12] disulfides,[13] SO_3,[14] H_2S,[15] and sulfur itself.[16] Despite the variety of the above-mentioned sulfur reagents utilized in the functionalizations of fullerenes, carbon

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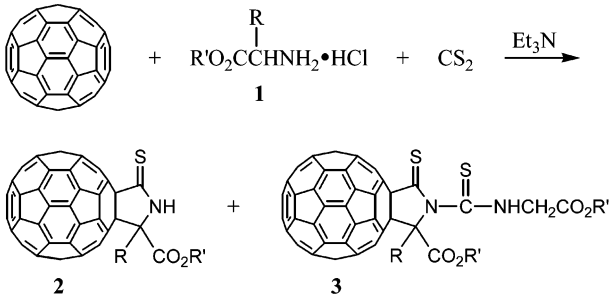
disulfide (CS_2), which is widely used as a solvent of fullerene compounds in NMR measurements and occasionally as a reaction media, has not been employed as a reagent in fullerene chemistry. It is known that reactions of CS_2 with amines and amino acids afford isothiocyanates and thioureas,[17] which are valuable functional groups in organic chemistry and have found wide usage in, for example, bioconjugate[18] and heterocyclic chemistry.[19] Functionalizations of C_{60} with amino acids and peptides to prepare biologically and pharmacologically active fullerene compounds are of great appeal to chemists.[20] In the continuation of our interest in fullerene chemistry,[21] we report the novel reactions of C_{60} with amino acid esters and CS_2 affording fullerene derivatives bearing amino acid, thioamide, and thiourea units. These fullerene compounds and their derivatives may have potential biological activities.

SCHEME 1. Reactions of C_{60} with Amino Acid Esters and CS_2



1a, **2a**, **3a**: R = H, R' = CH_3; **1b**, **2b**, **3b**: R = H, R' = CH_2CH_3; **1c**, **2c**, **3c**: R = H, R' = $(CH_2)_7CH_3$; **1d**, **2d**, **3d**: R = CH_3, R' = CH_2CH_3

TABLE 1. Yields of Products 2a−d and 3a−c Along with Recovered C_{60}

substrate	yield (%)[a] product **2**	yield (%)[a] product **3**	recovered C_{60} (%)
1a	30 (52)	4 (7)	42
1b	32 (58)	6 (11)	45
1c	35 (64)	5 (9)	45
1d	40 (70)	0 (0)	43

[a] Referred to isolated yield, the yield in parentheses is based on consumed C_{60}.

Results and Discussion

Glycine methyl ester hydrochloride (**1a**), glycine ethyl ester hydrochloride (**1b**), glycine octyl ester hydrochloride (**1c**), and L-alanine ethyl ester hydrochloride (**1d**) were chosen for our study. The reactions of C_{60} with 2 equiv of amino acid esters **1a**−**d** in CS_2 in the presence of triethylamine (Et_3N) afforded compounds **2a**−**d** as the major products and compounds **3a**−**c** as the minor products (Scheme 1). In these reactions, CS_2 behaved as a reagent as well as a solvent, meanwhile Et_3N acted as a base in the HCl-removal step and in the subsequent desulfurization and deprotonation steps (see below). Other amines such as pyridine and piperidine have been examined as the base, but were found to be ineffective in these reactions.

The yields of products **2a**−**d** and **3a**−**c** along with recovered C_{60} for the reactions of C_{60} with amino acid esters and CS_2 are listed in Table 1.

Amino acid ester and thioamide groups are integrated in adducts **2a**−**d**, and a third thiourea unit besides the functional groups in adducts **2a**−**d** is possessed by adducts **3a**−**c**. The identities of compounds **2a**−**d** and **3a**−**c** have been fully established by their MS, ^{1}H NMR, ^{13}C NMR, IR, and UV−vis spectral data. All MS spectra of **2a**−**d** and **3a**−**c** show the correct molecular weights. All of their UV−vis spectra display a characteristic absorption at 427−428 nm, typical for a 1,2-adduct of C_{60}. In the ^{1}H NMR spectra of **2a**−**d** and **3a**−**c**, besides the signals for the alkoxy and methine groups, all spectra display a broad singlet for the NH group. In the ^{13}C NMR spectra of **2a**−**d** and **3a**−**c**, besides the sp^3-C peaks for the two sp^3 carbons of the C_{60} cage and for the addends, two peaks at 197 and 168−170 ppm for the C═S (thioamide) and C═O group of **2a**−**d**, while four peaks at 198, 179, 168, and 167

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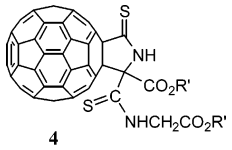

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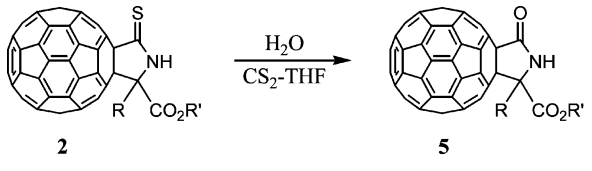
FIGURE 1. Another possible structure for compounds **3**.

SCHEME 2. Hydrolysis of Compounds 2



2a, **5a**: R = H, R' = CH_3; **2b**, **5b**: R = H, R' = CH_2CH_3;
2c, **5c**: R = H, R' = $(CH_2)_7CH_3$; **2d**, **5d**: R = CH_3, R' = CH_2CH_3

ppm for the two C═S (thioamide and thiourea) and two C═O groups of **3a**−**c**, and at least 45 partially overlapped peaks at 152−132 ppm due to the sp^2 carbons of the C_{60} skeleton have been observed, consistent with the C_1 symmetry of their molecular structures.

Another possible structure (**4**), which is consistent with the molecular weight of **3** and also a 1,2-adduct and might be formed from the reaction intermediates (vide infra), is shown in Figure 1. However, this possible structure for **3** is excluded because compound **4** should give two broad singlets for the two NH groups and the carbon-13 chemical shifts for the two C═S (thioamide) groups should be much closer.

Compounds **3** are not sensitive to moisture, and can be stored for a long time without any change. In contrast, products **2** are not stable and can be hydrolyzed during storage. Adducts **2** can be converted near quantitatively to products **5** in a mixture of CS_2−THF (9:1) in the presence of water at room temperature (Scheme 2).

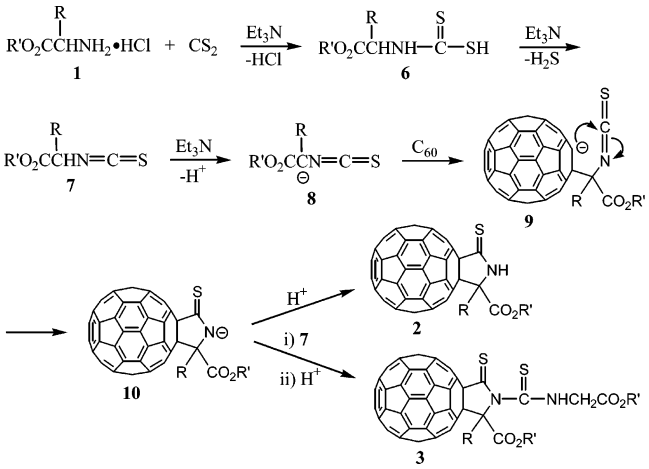
Compounds **5** are also fully characterized by MS, ^{1}H NMR, ^{13}C NMR, IR, and UV−vis spectral data. The ^{13}C NMR spectra of products **5** exhibited almost the same pattern as those of adducts **2** and **3** in the fullerenyl sp^2 carbons. In contrast, the δ_C of the fullerenyl sp^3 carbon connecting to the C═S group in adducts **2** (81−82 ppm) shifts upfield about 9 ppm after conversion to the C═O group in products **5** (72−74 ppm) and that of the C_{60}-attached sp^3 carbon in the addend shifts upfield 5−8 ppm, meanwhile the δ_C of another fullerenyl sp^3 carbon has no obvious change.

A possible reaction mechanism for the formation of products **2** and **3** is shown in Scheme 3.

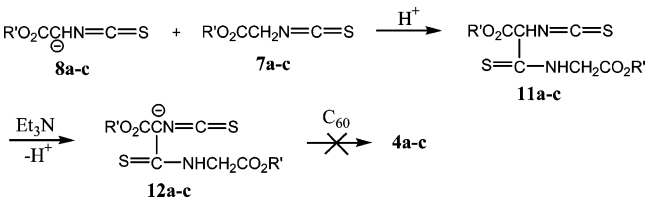
Triethylamine removes HCl from amino acid ester hydrochlorides **1**, and the resulting amino acid esters react with CS_2 to give dithiocarbamates **6**, which lose H_2S to afford isothiocyanates **7** under the influence of desulfurizing agent Et_3N. Deprotonation of **7** by Et_3N generates **8**. Carbanions **8** attack one of the C═C bonds of C_{60} to obtain fullerenyl anions **9**, which undergo intramolecular cylization to form thioamide anions **10**. Intermediates **10** can either be protonated to give adducts **2** or react with another molecule of **7**, followed by protonation to afford products **3**.

The chance for the reaction of **10** with a second molecule of **7** and then protonation should be much lower than that for the direct protonation of **10**, thus giving compounds **3** as the minor products. Furthermore, when R = CH_3, the steric hindrance of the methyl group prevents the reaction of **10d** with a second

SCHEME 3. Possible Mechanism for the Formation of Adducts 2 and 3



SCHEME 4. Possible Reason for the Failure of the Formation of Compounds 4



molecule of isothiocyanate **7d**, resulting in no formation of **3d**. The ratio of **2**/**3** was not changed during the reaction process, and control experiments showed that isolated **2** could not react with **1** and CS_2 in the presence of Et_3N to give **3**. These facts indicated that **3** was produced simultaneously with **2** from the same intermediates rather than from the secondary reactions of **2**, further substantiating the proposed reaction mechanism.

Carboanions **8a**−**c** could react with another molecule of isothiocyanates **7** to give **11a**−**c**, which could be deprotonated to afford **12a**−**c**. Probably due to the bulkiness of the attacking carboanions, **12a**−**c** failed to react with C_{60} to give compound **4a**−**c** (Scheme 4).

Conclusion

Carbon disulfide is widely used as a solvent of fullerene compounds in NMR measurements and occasionally as a reaction media. In this paper, we utilized carbon disulfide as a reagent for the first time in fullerene chemistry. It was found that the novel reactions of C_{60} with amino acid ester hydrochlorides and CS_2 in the presence of Et_3N afforded fullerene derivatives **2** and **3** bearing biologically active amino acid, thioamide, and thiourea units. The C═S(NH) group in the heterocycle fused to C_{60} in compounds **2** is sensitive to moisture and can easily be hydrolyzed to the C═O(NH) group, while the *N*-substituted analogues **3** are stable and not labile to hydrolysis. Study on the further functionalization of compounds **2** and **3**, and other reactions of C_{60} with CS_2 as a reagent, is in progress.

Experimental Section

Typical Procedure for the Synthesis of Compounds 2 and 3 by the Reaction of C_{60} with Amino Acid Esters and CS_2. A mixture of C_{60} (36.0 mg, 0.05 mmol) and amino acid ester

hydrochloride **1** (0.10 mmol) and dried Et_3N (0.5 mL) was stirred in anhydrous CS_2 (5 mL) under nitrogen atmosphere and at room temperature for 4 h. After evaporation of excess CS_2, the residue was washed with acetone to remove the nonfullerene byproducts, and then separated on a silica gel column with CS_2, then toluene, and finally toluene/ethyl acetate as the eluent to give unreacted C_{60}, product **3**, and product **2**, respectively. The yields along with recovered C_{60} are listed in Table 1.

2a: ^{1}H NMR (300 MHz, CS_2/DMSO-d_6) δ 11.86 (br s, 1H), 6.22 (s, 1H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 197.24 (*C*═S), 167.96 (*C*═O), 151.18, 150.18, 149.74, 147.96, 147.89, 147.72, 146.66, 146.31, 145.51, 145.41 (2C), 145.39, 145.14 (2C), 145.06 (2C), 144.87, 144.84, 144.80, 144.76, 144.74, 144.71, 144.68, 144.47, 144.34 (2C), 144.27, 144.20, 143.75, 143.71, 143.40, 143.31, 142.09, 142.02, 141.86 (2C), 141.84, 141.81, 141.57, 141.54, 141.41, 141.37, 141.11, 141.07, 141.03 (2C), 141.01, 140.85, 140.82 (2C), 139.59, 139.54, 139.16, 138.39, 135.85, 134.45, 133.11, 132.70, 81.71 (sp^3-C of C_{60}), 71.64 (N*C*H), 67.05 (sp^3-C of C_{60}), 51.66 (O*C*H$_3$); FT-IR (KBr) ν (cm^{-1}) 3373, 2945, 2920, 2853, 1750, 1509, 1432, 1253, 1213, 1183, 1154, 985, 894, 767, 651, 578, 527; UV−vis ($CHCl_3$) λ_{max} (nm) (log ϵ) 255 (5.14), 314 (4.65), 427 (3.57), 689 (2.57); MS (MALDI-TOF) *m*/*z* 851.

2b: ^{1}H NMR (300 MHz, CS_2/DMSO-d_6) δ 11.78 (br s, 1H), 6.11 (s, 1H), 4.32 (dq, J = 10.7, 7.2 Hz, 1H), 4.26 (dq, J = 10.7, 7.2 Hz, 1H), 1.25 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 197.12 (*C*═S), 167.57 (*C*═O), 151.28, 150.22, 149.82, 147.98, 147.87, 147.78, 146.63, 146.27, 145.50, 145.39 (2C), 145.38, 145.11, 145.09, 145.03 (2C), 144.80 (2C), 144.74 (3C), 144.68, 144.63, 144.45, 144.31 (2C), 144.24, 144.18, 143.71, 143.68, 143.37, 143.31, 142.06, 142.00, 141.84 (2C), 141.82, 141.81, 141.54, 141.50, 141.41, 141.36, 141.11, 141.04, 141.00 (2C), 140.99, 140.80, 140.77 (2C), 139.54, 139.51, 139.13, 138.17, 135.83, 134.49, 133.12, 132.70, 81.76 (sp^3-C of C_{60}), 71.37 (N*C*H), 67.03 (sp^3-C of C_{60}), 61.41 (O*C*H$_2$CH$_3$), 13.58 (OCH$_2$*C*H$_3$); FT-IR (KBr) ν (cm^{-1}) 3383, 2948, 2922, 2851, 1744, 1509, 1461, 1428, 1252, 1196, 1156, 1094, 1027, 864, 769, 651, 576, 527; UV−vis ($CHCl_3$) λ_{max} nm (log ϵ) 255 (5.05), 313 (4.57), 427 (3.52), 687 (2.47); MS (MALDI-TOF) *m*/*z* 865.

2c: ^{1}H NMR (300 MHz, CS_2/DMSO-d_6) δ 11.84 (br s, 1H), 6.12 (s, 1H), 4.30 (t, J = 6.5 Hz, 2H), 1.74−1.61 (m, 2H), 1.40−1.20 (m, 10H), 0.93 (t, J = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 196.93 (*C*═S), 167.37 (*C*═O), 151.05, 150.00, 149.60, 147.76, 147.64, 147.55, 146.40, 146.05, 145.28, 145.16 (2C), 145.14, 144.89 (2C), 144.81 (3C), 144.57 (2C), 144.49 (2C), 144.46, 144.41, 144.22, 144.08 (2C), 144.02, 143.92, 143.48, 143.47, 143.14, 143.05, 141.84, 141.77, 141.63, 141.61, 141.58 (2C), 141.32, 141.27, 141.16, 141.10, 140.89, 140.79, 140.77, 140.76, 140.73, 140.55 (3C), 139.32, 139.28, 138.89, 137.94, 135.65, 134.25, 132.90, 132.45, 81.54 (sp^3-*C* of C_{60}), 71.34 (NCH), 66.81 (sp^3-*C* of C_{60}), 65.23 (OCH$_2$), 31.11 (CH$_2$), 28.58 (CH$_2$), 28.56 (CH$_2$), 27.94 (CH$_2$), 25.32 (CH$_2$), 22.21 (CH$_2$), 13.57 (CH$_2$*C*H$_3$); FT-IR (KBr) ν (cm^{-1}) 3262, 2946, 2920, 2850, 1742, 1505, 1460, 1429, 1254, 1191, 1155, 1094, 893, 768, 728, 651, 578, 527; UV−vis ($CHCl_3$) λ_{max} (nm) (log ϵ) 256 (5.08), 313 (4.60), 427 (3.56), 688 (2.50); MS (MALDI-TOF) *m*/*z* 949.

2d: ^{1}H NMR (300 MHz, CS_2/DMSO-d_6) δ 11.85 (br s, 1H), 4.34 (dq, J = 10.3, 7.0 Hz, 1H), 4.23 (dq, J = 10.3, 7.0 Hz, 1H), 2.31 (s, 3H), 1.31 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 196.94 (*C*═S), 169.91 (*C*═O), 151.83, 150.58, 149.28, 148.90, 148.41, 147.38, 146.64, 146.28, 145.47, 145.40 (2C), 145.36, 145.16, 145.09, 145.03 (2C), 144.74, 144.66 (4C), 144.60, 144.50 (2C), 144.37, 144.33 (2C), 144.25, 143.83, 143.63, 143.35, 143.28, 142.08, 142.01, 141.89, 141.82 (3C), 141.55, 141.49 (2C), 141.38, 141.03, 140.98 (2C), 140.95 (3C), 140.70, 140.55, 139.54, 139.31, 138.90, 138.31, 135.53, 135.16, 133.73, 132.11, 82.26 (sp^3-C of C_{60}), 76.58 (N*C*CH$_3$), 71.82 (sp^3-C of C_{60}), 61.74 (O*C*H$_2$CH$_3$), 23.08 (C*C*H$_3$), 13.64 (OCH$_2$*C*H$_3$); FT-IR (KBr) ν (cm^{-1}) 3282, 2972, 2925, 2854, 1721, 1509, 1442, 1263, 1178, 1155, 1125, 1012, 894, 763, 651, 577, 526; UV−vis ($CHCl_3$) λ_{max} (nm) (log ϵ) 253 (5.11), 313 (4.65), 427 (3.58), 687 (2.49); MS (MALDI-TOF) *m*/*z* 879.

3a: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 13.01 (br s, 1H), 7.54 (s, 1H), 4.66 (dd, J = 18.6, 4.3 Hz, 1H), 4.58 (dd, J = 18.6, 4.3 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, CS_2/$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 197.76 (*C*═S), 179.07 (*C*═S), 167.98 (*C*═O), 167.37 (*C*═O), 150.66, 150.05, 149.40, 148.03, 147.95, 147.31, 147.11, 146.76, 146.14, 146.10 (2C), 146.01, 145.81 (2C), 145.72 (2C), 145.56, 145.53, 145.31, 145.28, 145.18, 145.17, 145.02, 144.97, 144.95 (2C), 144.74, 144.27, 144.19, 144.07, 144.01 (2C), 142.64, 142.56, 142.50, 142.47, 142.43 (2C), 142.11, 141.97, 141.96, 141.92, 141.76, 141.62, 141.58, 141.57, 141.51, 141.23, 141.19, 140.97, 140.12, 140.07, 140.03, 139.14, 135.86, 134.98, 134.80, 133.31, 85.89 (sp^3-C of C_{60}), 79.76 (N*C*H), 62.04 (sp^3-C of C_{60}), 52.66 (O*C*H$_3$), 52.26 (O*C*H$_3$), 48.05 (NH*C*H$_2$); FT-IR (KBr) ν (cm^{-1}) 3437, 2974, 2925, 1745, 1529, 1444, 1419, 1371, 1345, 1255, 1195, 1117, 1020, 894, 657, 581, 527. UV−vis ($CHCl_3$) λ_{max} (nm) (log ϵ) 256 (5.09), 314 (4.68), 428 (3.45), 688 (2.52); MS (MALDI-TOF) MS *m*/*z* 982.

3b: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 13.05 (br s, 1H), 7.57 (s, 1H), 4.67 (dd, J = 18.8, 4.3 Hz, 1H), 4.60 (dd, J = 18.8, 4.3 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 4.37 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, CS_2/$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 198.23 (*C*═S), 179.42 (*C*═S), 168.07 (C═O), 167.38 (C═O), 151.14, 150.59, 149.83, 148.47, 148.40, 147.70, 147.49, 147.10, 146.52, 146.49, 146.47, 146.40, 146.19 (2C), 146.10 (2C), 145.93 (2C), 145.68 (2C), 145.58, 145.56, 145.40, 145.36, 145.32 (3C), 144.66, 144.58, 144.44, 144.39, 144.37, 143.01, 142.94, 142.89, 142.85, 142.80 (2C), 142.49, 142.36 (2C), 142.30, 142.14, 142.02, 141.96, 141.95, 141.89, 141.58, 141.57, 141.34, 140.50, 140.45, 140.42, 139.39, 136.35, 135.44, 135.21, 133.64, 86.35 (sp^3-C of C_{60}), 79.92 (N*C*H), 62.66 (O*C*H$_2$CH$_3$), 62.46 (sp^3-C of C_{60}), 62.00 (O*C*H$_2$CH$_3$), 48.69 (NH*C*H$_2$), 14.31 (OCH$_2$*C*H$_3$), 14.12 (OCH$_2$*C*H$_3$); FT-IR (KBr) ν (cm^{-1}) 3441, 2975, 2925, 1746, 1530, 1442, 1418, 1371, 1347, 1255, 1195, 1115, 1019, 894, 769, 582, 527; UV−vis ($CHCl_3$) λ_{max} (nm) (log ϵ) 254 (5.08), 314 (4.67), 428 (3.56), 687 (2.48); MS (MALDI-TOF) *m*/*z* 1010.

3c: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 13.01 (br s, 1H), 7.56 (s, 1H), 4.65 (dd, J = 18.7, 4.5 Hz, 1H), 4.61 (dd, J = 18.7, 4.5 Hz, 1H), 4.36−4.23 (m, 4H), 1.78−1.73 (m, 2H), 1.69−1.62 (m, 2H), 1.43−1.24 (m, 20H), 0.91 (t, J = 6.9 Hz, 3H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, CS_2/$CDCl_3$, with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 197.98 (*C*═S), 179.17 (*C*═S), 167.82 (*C*═O), 167.13 (*C*═O), 151.12, 150.60, 149.79, 148.52, 148.39, 147.69, 147.48, 147.05, 146.51, 146.49, 146.48, 146.39, 146.18 (2C), 146.10 (2C), 145.91 (2C), 145.65 (2C), 145.58, 145.57, 145.39, 145.34, 145.32 (2C), 145.24, 144.64, 144.56, 144.43, 144.37 (2C), 143.04, 142.99, 142.92, 142.82, 142.79 (2C), 142.48, 142.34 (2C), 142.28, 142.12, 142.00 (2C), 141.94, 141.90, 141.58 (2C), 141.32, 140.45, 140.43, 140.42, 139.44, 136.33, 135.47, 135.21, 133.62, 86.36 (sp^3-C of C_{60}), 80.08 (N*C*H), 66.80 (O*C*H$_2$CH$_2$), 66.15 (O*C*H$_2$CH$_2$), 62.47 (sp^3-C of C_{60}), 48.70 (NH*C*H$_2$), 31.91 (CH$_2$), 31.87 (CH$_2$), 29.33 (3C, CH$_2$), 29.26 (CH$_2$), 28.71 (CH$_2$), 28.55 (CH$_2$), 26.11 (CH$_2$), 26.00 (CH$_2$), 22.83 (2C, CH$_2$), 14.20 (2C, *C*H$_3$); FT-IR (KBr) ν (cm^{-1}) (log ϵ) 3442, 2955, 2925, 2854, 1747, 1528, 1462, 1419, 1350, 1261, 1198, 1092, 892, 805, 723, 578, 527; UV−vis ($CHCl_3$) λ_{max} (nm) 254 (5.09), 313 (4.65), 428 (3.50), 686 (2.36); MS (MALDI-TOF) *m*/*z* 1178.

Typical Procedure for the Hydrolysis of Compounds 2 to Compounds 5. Compounds **2** (0.01 mmol) was added to a mixture of CS_2−THF (5 mL, 9:1) containing 1 μL of H_2O (0.056 mmol) and the reaction mixture was vigorously stirred at room temperature

for 8 h. After evaporation of excess CS_2, the residue was separated on a silica gel column with CS_2/THF as the eluent to give product **5**. The yields of **5a**−**d** were 93%, 92%, 93%, and 90%, respectively.

5a: ^{1}H NMR (300 MHz, CS_2/DMSO-d_6) δ 9.86 (br s, 1H), 5.95 (s, 1H), 3.99 (s, 3H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 169.39 (*C*═O), 168.96 (*C*═O), 151.61, 149.74, 149.63, 148.41, 147.16, 146.90, 146.47, 146.05, 145.33 (2C), 145.28 (2C), 145.03 (4C), 145.01, 144.69 (2C), 144.60 (3C), 144.50, 144.43, 144.36, 144.27, 144.24, 144.21, 143.55 (2C), 143.28, 143.23, 142.09, 142.03, 141.73 (2C), 141.70 (2C), 141.32, 141.25 (2C), 141.21, 141.07, 140.96, 140.94, 140.90 (3C), 140.81, 140.75, 139.86 (2C), 139.14, 138.36, 135.57, 134.36, 134.23, 133.64, 72.54 (sp^3-C of C_{60}), 66.27 (sp^3-C of C_{60}), 64.24 (N*C*H), 51.59 (O*C*H$_3$); FT-IR (KBr) ν (cm^{-1}) 3387, 2921, 2853, 1724, 1714, 1430, 1368, 1214, 1183, 1059, 576, 526; UV−vis ($CHCl_3$) λ_{max} (nm) (log ϵ) 256 (5.07), 312 (4.54), 427 (3.55), 688 (2.86); MS (MALDI-TOF) *m*/*z* 835.

5b: ^{1}H NMR (300 MHz, CS_2/DMSO-d_6) δ 9.82 (br s, 1H), 5.86 (s, 1H), 4.39 (dq, J = 10.6, 7.1 Hz, 1H), 4.33 (dq, J = 10.6, 7.1 Hz, 1H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent) δ 168.86 (*C*═O), 168.75 (*C*═O), 151.54, 149.65 (2C), 148.28, 147.15, 146.78, 146.36, 145.91, 145.24, 145.20, 145.16 (2C), 145.13, 144.92 (2C), 144.91, 144.87, 144.59, 144.57, 144.50 (3C), 144.38, 144.28, 144.25, 144.16, 144.12, 144.08, 143.46, 143.45, 143.13, 143.11, 141.97, 141.92, 141.62 (2C), 141.57 (2C), 141.22, 141.16, 141.14, 141.07, 140.98, 140.87, 140.85, 140.81, 140.79 (2C), 140.69, 140.58, 139.79, 139.77, 139.05, 138.05, 135.53, 134.26, 134.16, 133.39, 72.40 (sp^3-C of C_{60}), 66.17 (sp^3-C of C_{60}), 63.94 (N*C*H), 60.97 (O*C*H$_2$CH$_3$), 13.52 (OCH$_2$*C*H$_3$); FT-IR (KBr) ν (cm^{-1}) 3391, 2924, 2853, 1734, 1720, 1461, 1427, 1374, 1199, 1116, 1026, 576, 527; UV−vis ($CHCl_3$) λ_{max} (nm) (log ϵ) 255 (5.01), 313 (4.52), 427 (3.47), 692 (2.44); MS (MALDI-TOF) *m*/*z* 849.

5c: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 8.05 (br s, 1H), 5.98 (s, 1H), 4.29 (t, J = 6.5 Hz, 2H), 1.64−0.84 (m, 15H); ^{13}C NMR (75 MHz, CS_2/$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 171.91 (*C*═O), 169.53 (*C*═O), 151.65, 149.47, 149.19, 148.10, 147.49 (2C), 147.35, 147.04, 146.35, 146.28, 146.27 (2C), 146.01 (3C), 145.97, 145.89, 145.67, 145.64, 145.60 (2C), 145.48, 145.43, 145.31, 145.25, 145.18 (2C), 144.87, 144.45, 144.38, 144.13, 144.06, 142.99, 142.95, 142.68 (2C), 142.64 (2C), 142.22, 142.19, 142.12, 142.07, 141.91, 141.82 (4C), 141.61 (2C), 141.55, 141.01 (2C), 140.13, 139.16, 136.56, 135.34, 135.17, 134.80, 72.65 (sp^3-C of C_{60}), 67.19 (sp^3-C of C_{60}), 66.80 (O*C*H$_2$), 65.44 (N*C*H), 31.84 (CH$_2$), 29.29 (2C, CH$_2$), 28.68 (CH$_2$), 26.10 (CH$_2$), 22.82 (CH$_2$), 14.19 (CH$_2$*C*H3); FT-IR (KBr) ν (cm^{-1}) 3427, 2922, 2851, 1738, 1723, 1522, 1461, 1426, 1375, 1194, 1123, 1026, 725, 576, 527; UV−vis ($CHCl_3$) λ_{max} (nm) (log ϵ) 255 (5.10), 312 (4.57), 427 (3.52), 691 (2.46); MS (MALDI-TOF) MS *m*/*z* 933.

5d: ^{1}H NMR (300 MHz, CS_2/DMSO-d_6) δ 9.72 (br s, 1H), 4.32 (dq, J = 10.3, 7.1 Hz, 1H), 4.23 (q, J = 10.3, 7.1 Hz, 1H), 2.24 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent, all 1C unless indicated) δ 171.33 (*C*═O), 169.33 (*C*═O), 151.59, 150.02, 149.85, 149.18, 147.68, 146.44, 146.38, 146.01, 145.30, 145.27, 145.24 (2C), 145.03, 144.97 (2C), 144.95 (2C), 144.84, 144.67, 144.59, 144.57, 144.51, 144.50, 144.35, 144.26 (3C), 144.17, 143.68, 143.43, 143.26, 143.14, 142.09, 142.01, 141.72 (2C), 141.68 (2C), 141.31 (2C), 141.24, 141.19, 141.03, 140.96, 140.90, 140.87, 140.85 (2C), 140.70, 140.46, 139.85, 139.66, 138.85, 138.31, 135.33, 135.07, 134.82, 133.07, 73.56 (sp^3-C of C_{60}), 71.43 (NC*C*H$_3$), 68.64 (sp^3-C of C_{60}), 61.45 (O*C*H$_2$CH$_3$), 23.42 (C*C*H$_3$), 13.61 (OCH$_2$*C*H$_3$); FT-IR (KBr) ν (cm^{-1}) 3404, 2922, 2852, 1736, 1715, 1461, 1428, 1380, 1260, 1202, 1127, 1016, 575, 527; UV−vis ($CHCl_3$) λ_{max} (nm) (log ϵ) 255 (5.05), 312 (4.53), 427 (3.44), 691 (2.48); MALDI-TOF MS *m*/*z* 865.

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Supporting Information Available: MS, ^{1}H NMR, ^{13}C NMR, IR, and UV−vis spectra of compounds **2a**, **3a**, and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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