Acylation of 2,5-Dimethoxycarbonyl[60]fulleropyrrolidine and Synthesis of Its Multifullerene Derivatives

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2,5-Dimethoxycarbonyl[60]fulleropyrrolidine (**1**) is acylated with various chlorocarbonyl compounds to give fullerene derivatives with the general formula C_{60}(MeOOC*C*H)$_2$NC(O)R, R = $(CH_2)_5$Br, $(CH_2)_8$C(O)Cl (**3**), $(CH_2)_4$C(O)Cl, or *cis*-C_6H_4(C(O)Cl. The monoacylated sebacoyl derivative **3** readily reacts with alcohols and amines such as methanol, diethylamine, glycine methyl ester, and aza-18-crown-6 through the remaining chlorocarbonyl group. Chromatography of **3** on silica gel converts it into the corresponding acid C_{60}(MeOOC*C*H)$_2$NC(O)$(CH_2)_8$COOH (**4**). Treating **4** with PCl_5 regenerates the precursor **3** quantitatively. Piperazine reacts with **4** in the presence of DCC and BtOH to form a bisfullerene derivative in which two sebacoyl chains and the piperazine act as the bridge between two molecules of **1**. Other molecules with multifunctional groups react with **4** similarly to form multifullerene derivatives. NMR data indicate that the rotation of the relatively bulky phthaloyl group is hindered around the amide bond N−C(O), the rotation barrier of which is 15.06 kcal/mol. The relative stereochemistry of the 2,5-dimethoxycarbonyl groups is established by ^{1}H NMR spectra and further confirmed by resolution of the enantiomeric 2,5-*trans*-isomer of the starting material **1**.

Functionalization of fullerenes is one of the major strategies in exploring the practical use for fullerenes. Much success has been achieved.[1,2] Fullerene derivatives have been shown to exhibit many interesting properties which are promising in materials sciences and/or life sciences.[3,4] [60]Fulleropyrrolidines are frequently employed in these studies.[5] Most [60]fulleropyrrolidines are prepared by the well-known 1,3-dipole addition method.[6] Primary and secondary amines are usually incorporated into C_{60} by this method together with a carbonyl compound. Tertiary amines react with fullerene photochemically to give [60]fulleropyrrolidines directly.[7] Isomerically pure multiadducts of [60]fulleropyrrolidines have been reported.[8]

Although a large number of fulleropyrrolidines have been reported in the literature, chemical reactions or further functionalization of these compounds is still relatively rare.[9] The reactivity of the functional groups in fulleropyrrolidine is sometimes quite different from that of the functional groups in the non-fullerene analogues. For example, the fulleropyrrolidine N is several orders of magnitude less basic than the corresponding pyrrolidine N, and alkylation of the N is quite difficult under normal conditions.[10] In the synthesis of compounds with multifullerene cages, almost all the known multifullerene compounds with more than two C_{60} cages are derived from methanofullerenes.[11] To our knowledge, [60]fulleropyrrolidine has not been applied to the synthesis of multifullerenes except the dumbbells.[12]

We have reported the photochemical reaction between C_{60} and amino acid esters.[13] Irradiation of glycine methyl ester or iminodiacetic methyl ester with C_{60} yields 2,5-dimethoxycarbonyl[60]fulleropyrrolidine (**1**) (Scheme 1). The mechanism of this photochemical reaction is complicated. Foote et al. have unambiguously shown that singlet oxygen initiates the above radical reaction.[7] Our recent results suggest the involvement of a 1,3-dipole which is generated through the reaction of singlet oxygen and iminodiacetic methyl ester.[14] Here we report the

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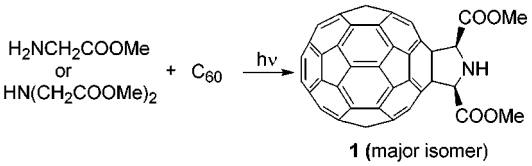
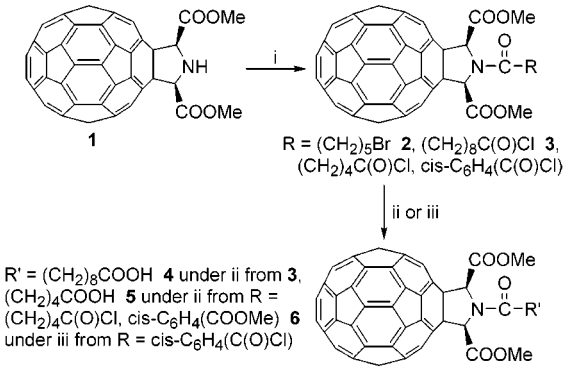
Scheme 1



1 (major isomer)

Scheme 2[a]



[a] Reagents and conditions: (i) pyridine and 6-bromohexanoyl chloride for **2**, sebacoyl chloride for **3**, adipoyl chloride for **5**, phthaloyl chloride for **6**; (ii) silica gel column; (iii) MeOH.

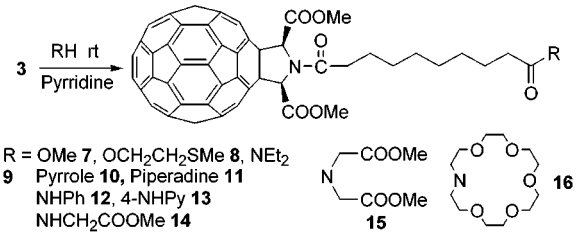
further functionalization of compound **1** through the acylation of the imino group, and the synthesis of bis-, tris-, tetrakis-, and hexakisfullerene compounds derived from **1**.[15]

Results and Discussion

Acylation of Compound 1. The [60]fulleropyrrolidine **1** can be acylated with various acyl chlorides (Scheme 2). Treating compound **1** with excess 6-bromohexanoyl chloride produces compound **2**. The addition of dichlorocarbonyl derivatives to **1** easily stops at the monoacylated stage. The symmetrical bisfullerene derivative cannot be obtained simply by varying the ratio of **1** and the dichlorocarbonyl. Even when a large excess of **1** is used, the major product is the monoacylated derivative still. Heating the reaction at 60 °C does not improve the situation, but only results in partial decomposition of **1** into C_{60}. The reactivity of the remaining acyl chloride decreases significantly once a C_{60} moiety is introduced through the first acyl chloride. This behavior is different from that of the reaction between isophthaloyl or terephthaloyl chloride and the unsubstituted [60]fulleropyrrolidine $C_{60}(CH_2NHCH_2)$, the main product of which is the bisfullerene derivative in a stoichiometric reaction.[12a] The reactivity difference is in agreement with the fact that a solid sample of **1** can be stored for months without noticeable change, whereas solid $C_{60}(CH_2NHCH_2)$ easily polymerizes due to the addition of the imino group to the double bonds of neighboring molecules.

The monoacylated species from the dichlorocarbonyls such as **3** are not isolated. They are easily converted to the more stable acid or methyl ester. The acidic derivatives **4** and **5** are produced upon chromatography of the corresponding monoacylated precursor. Water absorbed on the silica gel effectively hydrolyzes the acyl chloride. The presence of the long alkyl chains results in good solubility for these derivatives and facilitates elution on the column by chloroform. As much as 60 mg of the sebacoyl derivative may be dissolved in 1 mL of chloroform.

Scheme 3



Synthesis of Sebacoylmonofulleropyrrolidines. The preference of the dichlorocarbonyls for monoacylation toward **1** provides a handy method for attaching other substituents onto the molecule. The monoacylated sebacoyl derivative **3** is more soluble than the adipoyl and phthaloyl derivatives and is chosen for further functionalizations. Isolation of the intermediate **3** is not necessary. After sebacoyl is stirred with **1** for 24 h, an excess amount of the desired nucleophile is added into the reaction mixture. Stirring the resulting solution for another 5 h usually completes the second acylation. Since a large excess of sebacoyl chloride is used, it is difficult to fully separate other sebacoyl derivatives from the fullerene derivative by flash chromatography. However, such impurities can be removed by washing the crude product with methanol or by first dissolving the crude product in a minimum amount of chloroform and then adding methanol to cause precipitation. The final yields can reach more than 80% in most cases based on the starting material **1**.

Both alcohol and amine can act as the second-stage nucleophiles (Scheme 3). Only two alcohols, methanol and 3-(methylthio)-1-propanol, are tested, but others should react similarly. Diethylamine, pyrrole, piperadine, and 4-aminopyridine are all strong bases. It is possible for them to react with C_{60} directly through the known nucleophilic addition.[16] The monoaddition product of aza-18-crown-6 to C_{60} has been reported.[17] Under the present conditions such a reaction does not take place. The byproduct HCl of the acylation may have helped to prevent this process. It neutralizes part of the amine to form the ammonium salt R_2NH_2Cl, which forms a slightly basic buffer with the excess amine. In such a buffer solution the amines are probably not reactive enough to add to C_{60} directly. As depicted in Scheme 1 glycine methyl ester and iminodiacetic methyl ester react with C_{60} to form **1** at pH values around 8. To avoid such photoinduced reactions, the reaction flask is wrapped with aluminum foil and kept under a nitrogen atmosphere.

The sebacoyl acid derivative **4** is another useful synthon for further functionalization. Since it can be isolated

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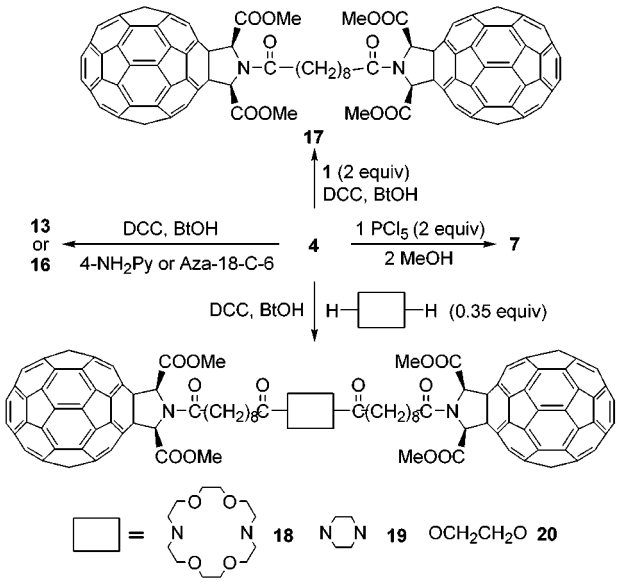
Scheme 4



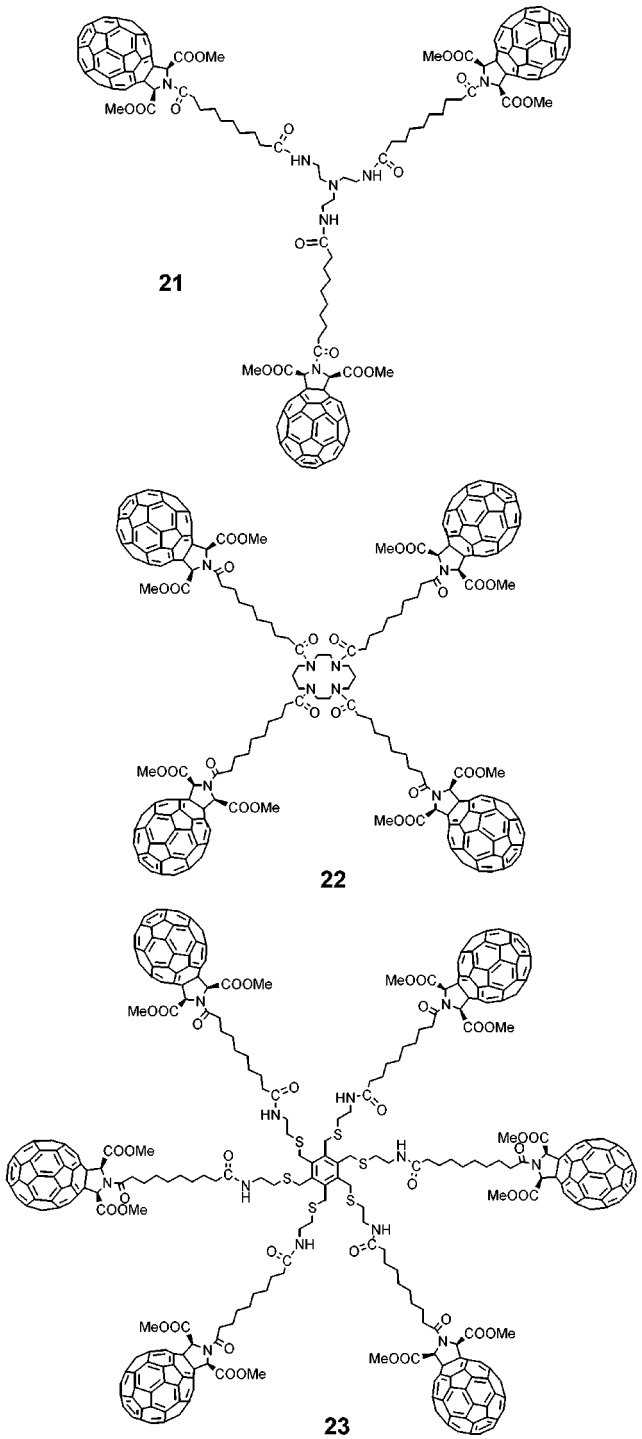
in its pure form, it offers certain advantages over the intermediate **3**. In the presence of DCC and BtOH those compounds in Scheme 3 such as **13**, **14**, and **16** can be prepared efficiently starting from **4** (Scheme 4). Compared to the one-pot synthesis in Scheme 3, much less of the somewhat expensive aza-18-crown-6 is required in the preparation of **16**. Most of the aza-18-crown-6 is consumed by the excess sebacoyl in the Scheme 3 procedure. Treating **4** with PCl_5 regenerates its precursor **3**. The so-formed **3** is free of excess sebacoyl chloride, and reacts with methanol to give the methoxy derivative **7** quantitatively.

Synthesis of Multifulleropyrrolidines. The bisfullerene derivatives **18**−**20** are prepared by treating **4** with the corresponding bifunctional bridging molecule in a 2:1 ratio in the presence of DCC and BtOH (Scheme 4). In the earlier Scheme 3 symmetrically acylated compounds such as **17** cannot be formed because of the presence of a large excess of sebacoyl chloride in the reaction mixture. Similarly compounds with multifunctional bridging groups react with **4** to give multifullerene compounds **21**, **22**, and **23** (Scheme 5). The reaction time for assembly varies from 4 days for the bisfullerenes to 5 weeks for the hexakisfullerene. The major byproducts of the reactions are unreacted **4** and dark materials stuck on the silica column.

Rotation of the Amide Bond in the Acylated Fulleropyrrolidine. The rotation of the phthaloyl group in compound **6** is hindered due to its relatively bulky size. Its NMR spectrum is quite temperature sensitive (Figure 1). At −10 °C the rotation of the phthaloyl moiety is virtually frozen on the NMR time scale. Three separate methoxy signals and two different pyrrolidine ring hydrogens are detected. As the temperature increases, the rotation gradually speeds up and the signals become broad. At 50 °C the two methoxy groups coalesce into a somewhat broad signal at 3.88 ppm, which is as expected around the average of their chemical shifts at −20 °C. In addition, the two pyrrolidine hydrogens become an obscure hump centered at 6.42 ppm. The process is fully reversible in the temperature range studied.

The phthaloyl rotation can occur about either the N−C(O) bond (i) or the (O)C−Ar bond (ii) as shown in

Scheme 5. Structures of Multifullerene Compounds



Scheme 6. The amide bond N−C(O) is well-known to have partial double bond character due to delocalization of the lone pair of N into the π-bond of the carbonyl. The preferred stereo arrangement of the carbonyl group is thus parallel to the pyrrolidine plane rather than perpendicular. The repulsion between the lone pair on the nitrogen and the carbonyl group also leads to the parallel conformation as shown by MM2 calculation. In this conformation the 2,5-positions of the pyrrolidine are nonequivalent. So the rotation of N−C(O) (i) is essential for the two methoxy groups and the two methyne hydrogens on the pyrrolidine ring to become equivalent. From the dynamic NMR experiment as shown in Figure

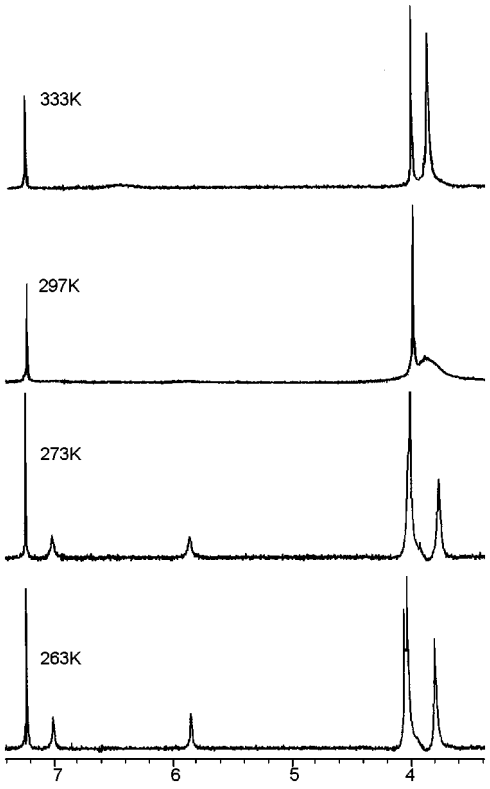
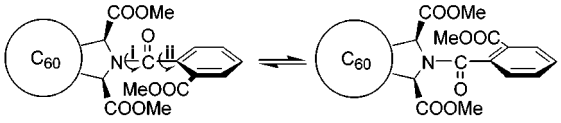


Figure 1. ^{1}H NMR spectrum of compound **6** at different temperatures.

Scheme 6. Possible Rotation Pathways of Compound 6



2, the rotation barrier can be calculated as 15.06 kcal/mol by using the well-established method.[18] For the less sterically demanding sebacoyl and adipoyl derivatives, the barrier of the same rotation is apparently smaller and the 2,5-positions are equivalent at rt.

NMR Data of the Multifullerene Compounds. In the ^{13}C NMR spectra of the multifullerenes all the fullerene carbons are similar in terms of both their chemical shifts and number of signals. This indicates that the different bridges have no noticeable effect on the distant C_{60} cage. The ^{1}H NMR data indicate that steric hindrance increases as the number of C_{60} cages increases in the molecule. The spectra of the bisfullerenes are well resolved. For the trisfullerene **21** the three ethylene groups attached to the central nitrogen show broad signals at rt while the other parts of the molecule still exhibit the same pattern as those of the bisfullerenes. For the tetrakisfullerene **22** all the signals are broad at rt, especially those of the azacrown and groups close to it. At 50 °C the methoxy and the methyne groups become sharp and the CH_2 adjacent to the C_{60} becomes a clear triplet, all of which are at the less crowded outer edge of the molecule. Other groups remain broad at this temperature. This indicates that the steric hindrance mainly originates from the center of the molecule. Heating the solution to 100 °C did not produce any further change (in *o*-$C_6D_4Cl_2$). For the hexakisfullerene **23** all the signals are broad at rt. At 50 °C the CH_2 adjacent to C_{60} becomes a broad but recognizable triplet. MM2 modeling confirms that the center of the molecule is crowded but the C_{60} cages are well separated from each other for these molecules. These temperature-dependent NMR spectra effectively rule out the possibility that the broadness of the signals of the multifullerene derivatives is due to mixtures of 2,5-*cis*- and 2,5-*trans*-isomers.

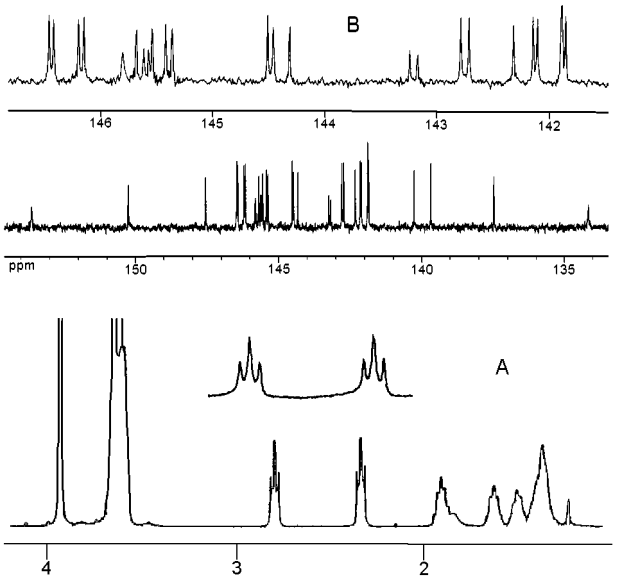


Figure 2. ^{1}H (A) and ^{13}C (B) NMR spectra of compound **16**.

NMR Evidence of the 2,5-*cis* Geometry of the Fulleropyrrolidines. The NMR data indicate that the two methoxycarbonyls at the 2,5-positions of the acylated pyrrolidines are in the *cis* configuration. Similar ^{13}C NMR patterns are observed for all the acylated [60]fulleropyrrolidines. Figure 2B shows the spectrum of the aza-18-crown-6 derivative **16** as an example. There are 30 separate signals in the region from 130 to 160 ppm. The signal at 141.80 is broad due to two overlapped signals. Thus, the actual number of fullerene signals is 32 including the two equivalent sp^3 carbon signals at 71.19 ppm. This indicates C_s symmetry; i.e., the 2,5-methoxycarbonyls are *cis* to each other. The C_2 symmetric 2,5-*trans*-isomer should exhibit 30 fullerene signals as observed for other related fullerene compounds.[19]

The ^{1}H NMR spectra also suggest the 2,5-*cis* geometry for the acylated [60]fulleropyrrolidines (Figure 2A). Hill and Chan reported that the NMR signals of the methylene protons attached to the nitrogen are diagnostic of the relative geometry of identically α,α′-disubstituted heterocyclic amines such as the *N*-benzyl-2,5-dimethylpyrrolidine.[20] The two protons are magnetically equivalent in the *cis*-isomer, and nonequivalent in the *trans*-isomer, exhibiting germinal coupling. The method has been successfully used to assign the *N*-ethyl-2,5-dimethyl-[60]fulleropyrrolidine as the 2,5-*trans* geometry.[21] The acylated [60]fulleropyrrolidines here, except the phthaloyl derivative **6**, which does not have a methylene group, all

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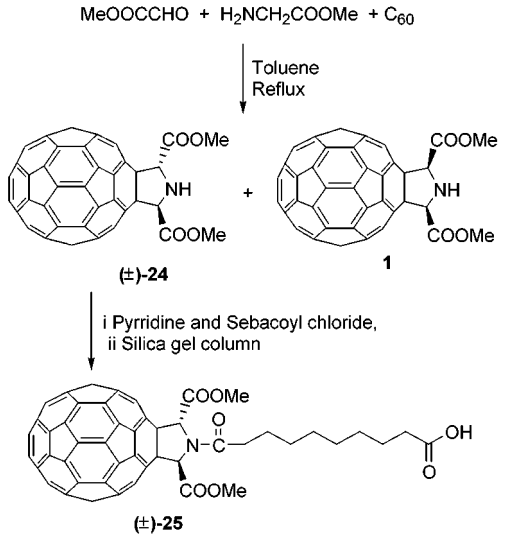
show triplets for the methylene protons adjacent to an acyl group. As shown in Figure 2 the aza-18-crown-6 derivative **16** exhibits two triplets at 2.82 and 2.36 ppm, which can be assigned to the two methylene groups adjacent to the electron-withdrawing C_{60} and the aza-18-crown-6, respectively. Their different chemical shifts indicate that the influence of the fulleropyrrolidine fragment is significant on the magnetic environment of the adjacent CH_2. Yet no germinal coupling is observed for this CH_2 group as would be expected for the 2,5-*trans*-isomer, thus supporting the above 2,5-*cis* assignment.

Stereochemistry. The stereochemistry of symmetrically 2,5-disubstituted fulleropyrrolidines has been a controversial issue. Several criteria have been used to assign the relative positions of the 2,5-substituents, but opposite conclusions were reported. Wilson et al. prepared a series of 2,5-disubstituted fulleropyrrolidines by using 1,3-dipoles derived from amino acids and aldehydes. On the basis of known ylide stereoselectivity, they assigned the main product as the 2,5-*cis*-isomer.[22] Nogami et al. questioned this assignment and suggested the compound as the 2,5-*trans*-isomer on the basis of the chemical shift difference of the 2,5-pyrrolidine ring protons.[23] Later Schuster and Wilson et al. reclaimed the 2,5-*cis* assignment by treating a mixture of 2,5-*cis*- and 2,5-*trans*-fulleropyrrolidines with chiral isocyanate and resolving the resulting diastereoisomers.[24]

We have tentatively assigned compound **1** as the 2,5-*trans*-isomer previously.[13] The main criterion at the time was the number of fullerene skeleton signals, 32 for the C_2 symmetric 2,5-*trans*-isomer and 30 for the C_s symmetric 2,5-*cis*-isomer. Overlapping of the signals is a serious problem of this criterion. The assignment is in agreement with their R_f values, i.e., smaller R_f for the presumed 2,5-*cis*-isomer than that of the presumed 2,5-*trans*-isomer. Yet the above NMR data of acylated [60]-fulleropyrrolidines, in particular the observed triplet of the CH_2 protons adjacent to the pyrrolidine amide group, strongly support the 2,5-*cis* symmetry according to the Hill and Chan *cis*/*trans* rule mentioned earlier.[19] The present result thus indicates that either our original assignment is wrong or a steric transformation process is involved during the acylation reaction.

To assign the stereochemistry of the starting material compound **1** conclusively, we investigated the thermal reaction between C_{60} and the 1,3-dipole derived from glycine methyl ester and methyl glyoxylate (Scheme 7). Unlike the photochemical reaction with glycine methyl ester, which yields mainly one isomer, i.e., compound **1**, the thermal reaction gave both the 2,5-*cis*- and 2,5-*trans*-isomers, and the ratio of the two can be controlled by changing the solvent. In pure toluene the isomer with the smaller pyrrolidine ring proton chemical shift (compound **1**) is the major product as in the case of the photochemical reaction. In a mixture of toluene and methanol (10:1) the major product depends on the reaction time. Longer refluxing time favors the isomer with a larger pyrrolidine ring proton chemical shift (compound **24**). The ratios between **1** and **24** are 1:3, 1:1, and 3:2 for periods of 6, 10, and 18 h, respectively. The two isomers

Scheme 7



(±)-25

can be separated by chromatography on silica gel. Surprisingly the more polar 2,5-*cis*-isomer **1** was eluted before the less polar 2,5-*trans*-isomer **24**. Similar deviations have been reported in other fullerene derivatives.[25] The expected different R_f values of the 2,5-*cis*- and 2,5-*trans*-stereoisomers have been used to assign the stereochemistry. Exceptions in these compounds mean that this criterion can be misleading.

Compound **24** reacts with sebacoyl chloride to give **25** (Scheme 7). The reaction is slower than that of compound **1** apparently due to increased steric hindrance. For the 2,5-*cis*-isomer, the acyl group can approach the pyrrolidine N from the face opposite the two methoxycarbonyl groups, whereas for the 2,5-*trans*-isomer, the approaching acyl group has to overcome the steric hindrance of one methoxycarbonyl group neighbor *cis* to it. In the ^{1}H NMR spectrum of **25** the two methoxy groups appear as two separate singlets (3.85 and 3.96 ppm) at rt. At 50 °C the two methoxy signals coalesce into a sharp singlet at 3.87 ppm. The CH_2 protons of the sebacoyl chain adjacent to the pyrrolidine amide group appear as a multiplet on the NMR spectrum, and the CH_2 protons adjacent to the carboxylic acid group appear as a triplet. These data clearly indicate a 2,5-*trans* arrangement. When Hill and Chan reported their *cis*/*trans* rule,[19] the examples in their work all had the diagnostic CH_2 group directly bonded to the pyrrolidine N. The present result means that the rule remains effective despite the presence of a carbonyl group between the diagnostic CH_2 and the pyrrolidine N. The increased distance between the 2,5-stereocenters and the CH_2 does not affect the validity of the rule for the present fulleropyrrolidines.

Unequivocal conclusion of the stereochemistry of **1** and **24** is obtained by resolving the enantiomers of the C_2 isomer **24** (2,5-*trans*) with a chiral HPLC column. Under exactly the same conditions, pure compound **1** (by ^{1}H NMR) shows just one signal as would be expected (Scheme 8), whereas pure compound **24** (by ^{1}H NMR) is separated into two signals with equal integrals. A mixture of **1** and **24** with a 0.7:1.1 ratio (by ^{1}H NMR) shows three signals. The first eluted peak has the same

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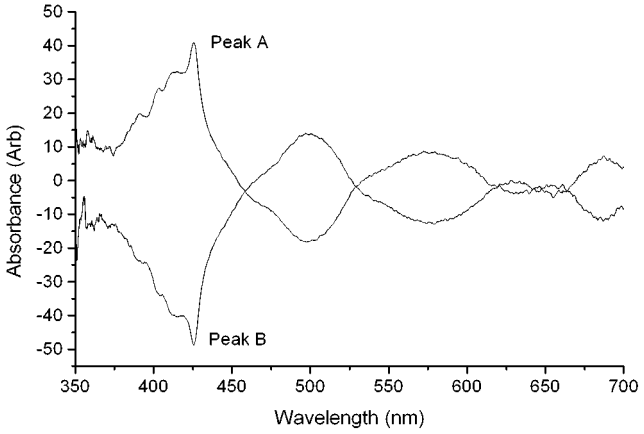
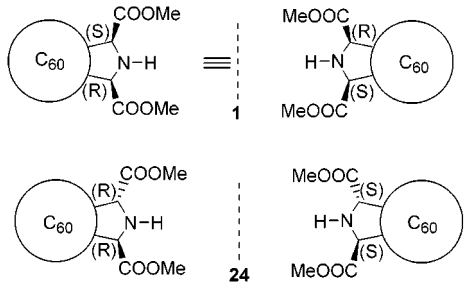


Figure 3. CD spectra of enantiomers of compound **24**.

Scheme 8. Optical Isomers of 2,5-Dimethoxycarbonyl[60]fulleropyrrolidine



retention time as that of pure **1**, and the second and the third are the same as those from **24**. The HPLC integrals between the first and the sum of the second and third are exactly the same as those from the NMR. The two signals from **24** were collected, and their circular dichroism (CD) spectra were obtained (Figure 3). As expected the two isomers showed almost mirror images from 350 to 700 nm. The 430 nm region is characteristic of fullerene derivatives with a 6,6-conjunction. The *meso*-**1** isomer (2,5-*cis*) does not have any significant CD in the same region. These data verify the structure assignment as depicted in the schemes.

Wilson and Schuster have proposed a sector rule for the assignment of the absolute configuration of groups attached to the fullerene core.[26] The method has been successfully applied to various fullerene compounds. According to this rule peak A should correspond to the 2,5-*trans*-*R*,*R*-enatiomer since it has a positive Cotton effect at 430 nm whereas peak B should correspond to the 2,5-*trans*-*S*,*S*-enatiomer since it has a negative Cotton effect at 430 nm. This assignment is in agreement with the fact that peak A was eluted before peak B in the (*S*)-*tert*-leucine-based chiral HPLC column, assuming the 2,5-*trans*-*S*,*S*-enatiomer has stronger interaction with the (*S*)-*tert*-leucine chiral column support.

Summary. Acylation has been shown to be an effective method for the functionalization of [60]fulleropyrrolidine. Both mono and dichlorocarbonyl derivatives can be used as the acylation reagents. The latter easily stops at the first stage, leaving the second acyl chloride for subsequent functionalization with other nucleophiles. A variety of fullerene derivatives may be prepared through this strategy. The sebacoyl acid derivative **4** serves as an excellent synthon for the synthesis of fullerene derivatives such as multi[60]fulleropyrrolidine compounds. The presence of the lipophilic sebacoyl chain greatly improves the solubility of these fullerene derivatives. All the [60]-fulleropyrrolidines here except **24** and **25** have the 2,5-*cis* configuration as determined by the chiral resolution method and the Hill and Chan NMR *cis*/*trans* criterion for 2,5-disubstituted pyrrolidines.[19]

Experimental Section

Compound **1** was prepared as reported.[13] All commercial reagents were used as received. 1,2,3,4,5,6-Hexakis(aminoethylsulfanylmethyl)benzene was prepared according to the literature method.[27] Toluene was distilled from sodium benzophenone ketyl. Chloroform was distilled from P_2O_5. Other solvents were used as received. All the acylation reactions were carried out in a similar way. The following describes the synthesis of the methyl ester of the sebacoyl-2,5-dimethoxycarbonyl[60]fulleropyrrolidine (**7**) as an example.

Sebacoyl chloride (300 mg, 1.26 mmol) was added to a stirred solution of **1** (85 mg, 0.097 mmol) and pyridine (2 mL) in freshly distilled toluene (100 mL). After the mixture was stirred for 24 h at rt, methanol (3 mL) was added to the mixture. The resulting solution was stirred for another 5 h. Throughout the reaction the flask was kept under nitrogen and wrapped with aluminum foil. The solvent was evaporated on a rotovap. The residue was extracted with toluene and chromatographed on a silica gel column (200−300 mesh, about 10 cm high and 2.5 cm in diameter). Toluene first eluted some unreacted **1** (less than 5 mg). Chloroform then eluted the product **7**. The solvent chloroform was evaporated. The residue was dissolved in 2 mL of chloroform and precipitated by adding methanol, then washed with methanol and petroleum ether (bp 30−60 °C), and finally dried under vacuum to give **7** as a brown powder (93 mg, 89% yield).

6-Bromohexanoyl Derivative of 2,5-Dimethoxycarbonyl[60]fulleropyrrolidine (2). 6-Bromohexanoyl chloride (500 mg, 2.3 mmol), compound **1** (85 mg, 0.1 mmol), and pyridine (5 mL) in toluene (100 mL) were mixed and stirred for 10 h at rt. The resulting solution was centrifuged before evaporation to remove insoluble byproducts. The product was purified by chromatography as above (87 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68−1.8 (m, 2H), 1.9−2.0 (m, 4H), 2.85 (t, 2H, J = 7.0 Hz), 3.50 (t, 2H, J = 6.6 Hz), 3.96 (s, 6H), 6.57 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.07 (CO), 168.97 (CO), 153.55, 150.14, 147.58, 146.48, 146.44, 146.22, 146.17, 145.78, 145.71, 145.62, 145.56, 145.44, 145.38, 144.52, 144.47, 144.28, 143.26, 143.19, 142.81, 142.74, 142.33, 142.16, 142.09, 141.90, 141.87, 140.29, 139.68, 137.48, 134.15, 70.26 (2CH), 53.04 (OMe), 34.14 (CH_2), 33.68 (CH_2), 32.58 (CH_2), 27.83 (CH_2), 24.12 (CH_2). FT-IR (microscope): 1748, 1678 cm^{-1}. MALDITOF-MS: *m*/*z* (rel intens) 1078 (82, M^+ + Na), 1055 (23, M^+), 880 (71), 820 (97), 720 (100, C_{60}^+). UV−vis: 256, 314, 430 nm. Anal. Calcd for $C_{72}H_{18}O_5NBr\cdot0.5H_2O$: C, 81.20; H, 1.80; N, 1.32. Found: C, 81.18; H, 1.96; N, 1.14.

Monoacylated Sebacoyl Derivative of 2,5-Dimethoxycarbonyl[60]fulleropyrrolidine (4). Sebacoyl chloride (300 mg, 1.26 mmol), compound **1** (85 mg, 0.097 mmol), and pyridine (2 mL) in toluene (100 mL) were mixed and stirred for 24 h as in the preparation general procedure. The red-brown solution was evaporated. The residue was extracted with toluene and chromatographed as above (95 mg, 93% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.39−1.7 (m, 10H), 1.8−2.0 (m, 2H), 2.36 (t, 2H, J = 7.2 Hz), 2.82 (t, 2H, J = 7.2 Hz), 3.95 (s, 6H), 6.57 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.97 (CO), 172.53 (CO), 169.02 (CO), 153.76, 150.20, 147.54, 146.45, 146.41, 146.18, 146.14, 145.78, 145.67, 145.54, 145.41, 145.35, 144.50, 144.47, 144.30, 143.24, 143.17, 142.78, 142.71, 142.31,

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142.14, 142.09, 141.88, 141.84, 140.25, 139.66, 137.46, 134.14, 71.22 (2C, sp^3), 70.25 (2CH), 52.98 (OMe), 34.38 (CH_2), 33.92 (CH_2), 29.26 (CH_2), 29.22 (CH_2), 29.14 (CH_2), 29.02 (CH_2), 25.03 (CH_2), 24.69 (CH_2). FT-IR (microscope): 1749, 1704, 1631 cm^{-1}. MALDITOF-MS: *m/z* (rel intens) 1086 (77, $M^+ + Na$), 880 (17), 820 (25), 720 (100, C_{60}^+). UV−vis: 255, 314, 429 nm. Anal. Calcd for $C_{76}H_{25}O_7N \cdot C_7H_8 \cdot H_2O$: C, 82.37; H, 3.25; N, 1.16. Found: C, 82.27; H, 3.06; N, 1.28.

Monoacylated Adipoyl Derivative of 2,5-Dimethoxycarbonyl[60]fulleropyrrolidine (5). Adipoyl chloride (2 g, 11 mmol), compound **1** (80 mg, 0.091 mmol), and pyridine (2 mL) in toluene (100 mL) were mixed and stirred for 24 h as in the preparation general procedure. The red-brown solution was evaporated. The residue was extracted with toluene and chromatographed as above (60 mg, 66% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.95 (m, 4H), 2.53 (t, 2H, J = 7.2 Hz), 2.87 (t, 2H, J = 7.2 Hz), 3.96 (s, 6H), 6.57 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.05 (CO), 171.97 (CO), 168.96 (CO), 153.50, 150.13, 147.56, 146.47, 146.42, 146.21, 146.16, 145.78, 145.70, 145.56, 145.42, 145.37, 144.51, 144.46, 144.28, 143.25, 143.16, 142.80, 142.73, 142.32, 142.15, 142.09, 141.87, 141.83, 140.28, 139.68, 137.48, 134.11, 71.20 (2C, sp^3), 70.25 (2CH), 53.06 (OMe), 41.35 (CH_2), 33.99 (CH_2), 28.90 (CH_2), 24.42 (CH_2). FT-IR (microscope): 1749, 1704, 1631 cm^{-1}. MALDITOF-MS: *m/z* (rel intens) 1030 (29, $M^+ + Na$), 820 (34), 720 (100, C_{60}^+).

Phthaloyl Derivative of 2,5-Dimethoxycarbonyl[60]-fulleropyrrolidine (6). Phthaloyl chloride (1.2 g, 5.91 mmol), compound **1** (85 mg, 0.097 mmol), and pyridine (2 mL) in toluene (100 mL) were mixed and stirred for 24 h, and then excess methanol (10 mL) was added. The resulting solution was treated as in the preparation general procedure (87 mg, 88% yield). ^{1}H NMR (200 MHz, $CDCl_3$, 253 K): δ 3.81 (s, 3H), 4.02 (s, 3H), 4.06 (s, 3H), 5.88 (s, 1H), 7.07 (s, 1H), 7.6−7.9 (m, 3H), 8.3 (d, 1H). ^{1}H NMR (200 MHz, $CDCl_3$, 323 K): δ 3.83 (s, 3H), 4.0 (br, 6H), 6.39 (v br, 2H), 7.60−7.8 (m, 3H), 8.2 (d, 1H). ^{1}H NMR (200 MHz, $CDCl_3$, 297 K): δ 3.88 (s, 6H), 4.01 (s, 3H), 5.89 (s, 1H), 7.02 (s 1H), 7.61−8.20 (m, 4H). ^{13}C NMR (100 MHz, 323 K): δ 170.01 (CO), 168.94 (CO), 165.95 (CO), 153.68, 150.51, 147.67, 146.58, 146.51, 146.29 146.26, 145.92, 145.82, 145.80, 145.70, 145.67, 145.54, 145.42, 144.62, 143.31, 142.87, 142.86, 142.43, 142.32, 142.09, 142.02, 141.97, 141.93, 140.29, 139.69, 137.38, 134.96, 132.92 (C), 131.00 (C), 130.04 (CH), 128.30 (CH), 127.89 (CH), 71.61 (2CH), 52.75 (OMe), 52.65 (OMe). ^{13}C NMR (100 MHz, 297 K): δ 170.04 (CO), 168.96 (CO), 165.80 (CO, br), 147.50, 146.41, 146.36, 146.13, 144.09, 145.80, 145.66, 145.52, 145.38, 145.26, 144.44 (br), 143.15, 142.80, 142.70, 142.25 (br), 142.15, 141.86, 141.79 (br), 140.12 (br), 139.56 (br), 137.10, 133.00 (C), 130.98 (C), 130.07 (CH), 128.07 (CH), 127.49 (CH), 72.43 (2C, sp^3), 70.33 (2CH), 52.81 (OMe). FT-IR (microscope): 1748, 1654 cm^{-1}. MALDITOF-MS: *m/z* (rel intens) 1041 (100, $M^+ + Na$), 720 (13, C_{60}^+). UV−vis: 257, 314, 430 nm. Anal. Calcd for $C_{75}H_{15}O_7N \cdot 0.5H_2O$: C, 85.71; H, 1.54; N, 1.33. Found: C, 85.39; H, 1.75; N, 1.19.

Methyl Ester of the Sebacoyl-2,5-dimethoxycarbonyl-[60]fulleropyrrolidine (7). Procedure 1 was as described in the general procedure. Procedure 2: To a stirred solution of **4** (80 mg, 0.075 mmol) in freshly distilled chloroform (60 mL) was added phosphorus pentachloride (31 mg, 0.15 mmol) at 0 °C. After the reaction mixture was stirred at 0 °C for 5 h, methanol (5 mL) was added, and the resulting solution was slowly warmed and stirred at rt for 5 h. The reaction mixture was evaporated to give a brown residue, which was extracted with toluene and chromatographed on a silica gel column as in the general procedure (77 mg, yield 95%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.39−1.75 (m, 10H), 1.84−2.0 (m, 2H), 2.32 (t, 2H, J = 7.2 Hz), 2.82 (t, 2H, J = 7.2 Hz), 3.67 (s, 3H) 3.95 (s, 6H), 6.57 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.19 (CO), 172.40 (CO), 168.99 (CO), 153.56, 150.17, 147.51, 146.41, 146.37, 146.15, 146.11, 145.74, 145.63, 145.55, 145.49, 145.37, 145.31, 144.46, 144.41, 144.25, 143.20, 143.13, 142.74, 142.67, 142.27, 142.10, 142.06, 141.83, 140.21, 139.62, 137.42, 134.09, 71.19 (2C, sp^3), 70.20 (2CH), 52.92 (OMe), 51.40 (OMe), 34.34 (CH_2), 34.04 (CH_2), 29.27 (CH_2), 29.21 (CH_2), 29.12 (CH_2), 29.08 (CH_2), 24.98 (CH_2), 24.89 (CH_2). FT-IR (microscope): 1741, 1677 cm^{-1}. MALDITOF-MS: *m/z* (rel intens) 1078 (42, $M^+ + 1$), 880 (17), 820 (51), 720 (100, C_{60}^+). UV−vis: 255, 313, 431 nm. Anal. Calcd for $C_{77}H_{27}O_7N \cdot H_2O$: C, 84.37; H, 2.67; N, 1.28. Found: C, 84.09; H, 2.52; N, 1.21.

2-(Methylthio)ethanol Ester of the Sebacoyl-2,5-dimethoxycarbonyl[60]fulleropyrrolidine (8). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.39−2.0 (m, 12H), 2.10 (s, 3H), 2.31 (t, 2H, J = 7.3 Hz), 2.5−2.62 (m, 2H), 2.82 (t, 2H, J = 7.2 Hz), 3.94 (s, 6H), 4.17 (t, 2H, J = 6.6 Hz), 6.54 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.71 (CO), 172.42 (CO), 168.99 (CO), 153.53, 150.17, 147.49, 146.40, 146.39, 146.14, 146.09, 145.73, 145.63, 145.54, 145.51, 145.48, 145.36, 145.30, 144.45, 144.41, 144.27, 143.19, 143.12, 142.73, 142,66, 142.27, 142.09, 142.05, 141.83, 141.79, 140.19, 139.62, 137.40, 134.11, 71.20 (2C, sp^3), 70.15 (2CH), 62.81 (OCH_2) 52.98 (OMe), 34.35 (CH_2), 34.25 (CH_2), 29.32 (CH_2), 29.24 (CH_2), 29.16 (CH_2), 29.03 (CH_2), 28.21 (CH_2), 24.99 (CH_2), 24.94 (CH_2), 15.52 (CH_3). FT-IR (microscope): 1748, 1678 cm^{-1}. MALDITOF-MS: *m/z* (rel intens) 1174 (20, $M^+ + Na$), 720 (100, C_{60}^+). UV−vis: 256, 313, 431 nm. Anal. Calcd for $C_{80}H_{33}O_7NS$: C, 83.39; H, 2.89; N, 1.22. Found: C, 83.00; H, 2.72; N, 1.15.

Diethylamine Amide of the Sebacoyl-2,5-dimethoxycarbonyl[60]fulleropyrrolidine (9). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.42−1.89 (m, 18H), 2.30 (t, 2H, J = 7.2 Hz), 2.82 (t, 2H, J = 7.3 Hz), 3.32 (m, 4H), 3.95 (s, 6H), 6.58 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.52 (CO), 172.36 (CO), 169.04 (CO), 153.58, 150.22, 147.54, 146.44, 146.40, 146.18, 146.13, 145.78, 145.66, 145.59, 145.55, 145.52, 145.40, 145.34, 144.49, 144.44, 144.30, 143.22, 143.16, 142.77, 142.70, 142.30, 142.13, 142.09, 141.87, 141.84, 140.24, 139.65, 137.45, 134.15, 71.29 (2C, sp^3), 70.21 (2CH), 52.99 (OMe), 42.02 (CH_2), 40.10 (CH_2), 34.40 (CH_2), 33.14 (CH_2), 29.52 (CH_2), 29.39 (CH_2), 29.28 (CH_2), 29.18 (CH_2), 25.48 (CH_2), 25.05 (CH_2), 14.44 (CH_3), 13.14 (CH_3). FT-IR (microscope): 1748, 1679, 1631 cm^{-1}. MALDITOF-MS: *m/z* (rel intens) 1141 (100, $M^+ + Na$), 880 (7.7), 820 (11.5), 720 (19.2, C_{60}^+). UV−vis: 255, 313, 430 nm. Anal. Calcd for $C_{80}H_{34}O_6N_2 \cdot H_2O$: C, 84.49; H, 3.19; N, 2.46. Found: C, 84.85; H, 2.98; N, 2.15.

Pyrrole Amide of the Sebacoyl-2,5-dimethoxycarbonyl-[60]fulleropyrrolidine (10). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.39−1.92 (m, 16H), 2.32 (t, 2H, J = 7.2 Hz), 2.82 (t, 2H, J = 7.2 Hz), 3.42 (t, 4H, J = 6.6 Hz), 3.95 (s, 6H), 6.57 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.47 (CO), 171.86 (CO), 168.98 (CO), 153.53, 150.19, 147.48, 146.38, 146.34, 146.12, 146.07, 145.73, 145.60, 145.53, 145.50, 145.47, 145.33, 145.28, 144.44, 144.39, 144.27, 143.17, 143.10, 142.71, 142.64, 142.25, 142.08, 142.03, 141.82, 141.78, 140.17, 139.60, 137.39, 134.11, 71.13 (2C, sp^3), 70.15 (2CH), 52.98 (OMe), 46.69 (CH_2), 45.63 (CH_2), 34.80 (CH_2), 34.36 (CH_2), 29.46 (CH_2), 29.35 (CH_2), 29.23 (CH_2), 29.10 (CH_2), 26.12 (CH_2), 25.01 (CH_2), 24.88 (CH_2), 24.41 (CH_2). FT-IR (microscope): 1748, 1678, 1631 cm^{-1}. MALDITOF-MS: *m/z* (rel intens) 1139 (100, $M^+ + Na$), 1117 (6, $M^+ + 1$). UV−vis: 256, 313, 430 nm. Anal. Calcd for $C_{80}H_{32}O_6N_2 \cdot 0.5H_2O$: C, 85.32; H, 2.96; N, 2.49. Found: C, 85.50; H, 2.83; N, 2.18.

Piperadine Amide of the Sebacoyl-2,5-dimethoxycarbonyl[60]fulleropyrrolidine (11). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.28−1.89 (m, 18H), 2.29 (m, 2H), 2.78 (t, 2H, J = 7.4 Hz), 3.35 (t, 2H, J = 5.4 Hz), 3.50 (t, 2H, J = 5.4 Hz), 3.91 (s, 6H), 6.54 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.48 (CO), 171.46 (CO), 168.01 (CO), 153.59, 150.22, 147.52, 146.43, 146.38, 146.19, 146.12, 145.77, 145.65, 145.57, 145.54, 145.51, 145.38, 145.33, 144.48, 144.44, 144.30, 143.22, 143.14, 142.76, 142.69, 142.30, 142.12, 142.08, 141.86, 141.82, 140.22, 139.64, 137.44, 134.13, 71.23 (2C, sp^3), 70.20 (2CH), 52.96 (OMe), 46.73 (CH_2), 42.62 (CH_2), 34.38 (CH_2), 33.42 (CH_2), 29.50 (CH_2), 29.46 (CH_2), 29.34 (CH_2), 29.25 (CH_2), 26.60 (CH_2), 25.59 (CH_2), 25.44 (CH_2), 25.04 (CH_2), 24.59 (CH_2). FT-IR (microscope): 1748, 1679, 1631 cm^{-1}. MALDITOF-MS: *m/z* (rel intens) 1153 (100, $M^+ + Na$), 720 (35, C_{60}^+). UV−vis: 256, 314, 430 nm. Anal. Calcd for $C_{81}H_{34}O_6N_2 \cdot 0.5H_2O$: C, 85.33; H, 3.09; N, 2.46. Found: C, 85.32; H, 3.03; N, 2.17.

Aminobenzene Amide of the Sebacoyl-2,5-dimethoxycarbonyl[60]fulleropyrrolidine (12). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.42−1.93 (m, 12H), 2.37 (t, 2H, J = 7.2 Hz), 2.82 (t, 2H, J = 7.2 Hz), 3.94 (s, 6H), 6.57 (s, 2H), 7.10−7.51 (m,

5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.06 (CO), 170.80 (CO), 168.67 (CO), 153.50, 150.07, 147.45, 146.39, 146.34, 146.11, 146.07, 145.71, 145.63, 145.46, 145.32, 145.27, 144.44, 144.37, 144.19, 143.17, 143.10, 142.73, 142.64, 142.24, 142.06, 141.97, 141.82, 141.79, 141.77, 140.21, 139.57, 137.42, 134.04, 128.89, 124.00 (CH), 119.53, 71.11 (2C, sp^3), 70.11 (2CH), 52.71 (OMe), 37.70 (CH_2), 34.23 (CH_2), 29.20 ($4CH_2$), 25.52 (CH_2), 24.96 (CH_2). FT-IR (microscope): 1747, 1652 cm^{-1}. MALDITOF-MS: *m*/*z* (rel intens) 1161 (100, $M^+ + Na$), 880 (21), 820 (17), 720 (17, C_{60}^+). UV−vis: 256, 314, 430 nm. Anal. Calcd for $C_{82}H_{30}O_6N_2 \cdot 1.5H_2O$: C, 84.45; H, 2.85; N, 2.40. Found: C, 84.27; H, 2.71; N, 2.34.

4-Aminopyridine Amide of the Sebacoyl-2,5-dimethoxycarbonyl[60]fulleropyrrolidine (13). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.40−1.92 (m, 12H), 2.43 (t, 2H, J = 7.2 Hz), 2.82 (t, 2H, J = 7.2 Hz), 3.94 (s, 6H), 6.57 (s, 2H), 7.53 (d, 2H, J = 6 Hz), 7.89(s, 1H), 8.49 (d, 2H, J = 5.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.68 (CO), 172.45 (CO), 169.03 (CO), 153.51, 150.34, 150.06, 147.57, 146.48, 146.42, 146.22, 146.17, 145.73, 145.69, 145.63, 145.56, 145.54, 145.42, 145.37, 144.50, 144.45, 144.26, 143.26, 143.19, 142.81, 142.75, 142.31, 142.13, 142.06, 141.89, 141.84, 140.27, 139.69, 137.41, 134.10, 113.63, 70.35 (2CH), 53.02 (OMe), 37.69 (CH_2), 34.37 (CH_2), 29.08 ($2CH_2$), 29.04 (CH_2), 28.98 (CH_2), 25.20 (CH_2), 24.92 (CH_2). FT-IR (microscope): 1745, 1666 cm^{-1}. MALDITOF-MS: *m*/*z* (rel intens) 1140 (61, $M^+ + 1$), 720 (100, C_{60}^+). UV−vis: 257, 313, 431 nm. Anal. Calcd for $C_{81}H_{29}O_6N_3 \cdot 0.5CHCl_3 \cdot H_2O$: C, 80.98; H, 2.54; N, 3.48. Found: C, 80.54; H, 2.63; N, 3.42.

Glycine Methyl Ester Derivative of the Sebacoyl-2,5-dimethoxycarbonyl[60]fulleropyrrolidine (14). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.39−1.92 (m, 12H), 2.27 (t, 2H, J = 7.2 Hz), 2.82 (t, 2H, J = 7.3 Hz), 3.78 (s, 3H), 3.95 (s, 6H), 4.06 (d, 2H, J = 5.2 Hz), 6.12 (s, 1H), 6.57 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.29 (CO), 172.50 (CO), 170.44 (CO), 169.03 (CO), 153.56, 150.19, 147.53, 146.44, 146.39, 146.18, 146.13, 145.77, 145.66, 145.58, 145.52, 145.52, 145.39, 145.34, 144.48, 144.43, 144.29, 143.22, 143.16, 142.76, 142,69, 142.30, 142.13, 142.08, 141.86, 141.83, 140.24, 139.65, 137.44, 134.14, 71.23 (2C, sp^3), 70.22 (2CH), 52.99 (OMe), 52.38 (OMe), 41.20 (CH_2), 36.34 (CH_2), 34.37 (CH_2), 29.28 (CH_2), 29.22 (CH_2), 29.20 (CH_2), 29.16 (CH_2), 25.51 (CH_2), 24.99 (CH_2). FT-IR (microscope): 1750, 1681, 1655 cm^{-1}. MALDITOF-MS: *m*/*z* (rel intens) 1157 (100, $M^+ + Na$), 880 (32), 820 (24), 720 (22, C_{60}^+). UV−vis: 257, 313, 431 nm. Anal. Calcd for $C_{79}H_{30}O_8N_2$: C, 83.58; H, 2.67; N, 2.47. Found: C, 83.36; H, 2.65; N, 2.04.

Iminodiacetic Methyl Ester Derivative of the Sebacoyl-2,5-dimethoxycarbonyl[60]fulleropyrrolidine (15). $_1$H NMR (200 MHz, $CDCl_3$): δ 1.39−1.92 (m, 12H), 2.32 (t, 2H, J = 7.2 Hz), 2.82 (t, 2H, J = 7.2 Hz), 3.72 (s, 3H), 3.78 (s, 3H), 3.95 (s, 6H), 4.19 (s, 2H), 4.20 (s, 2H), 6.57 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.51 (CO), 172.44 (CO), 169.84 (CO), 169.41 (CO), 169.00 (CO), 153.59, 150.22, 147.52, 146.43, 146.39, 146.16, 146.12, 145.77, 145.65, 145.58, 145.54, 145.51, 145.39, 145.33, 144.48, 144.43, 144.29, 143.21, 143.15, 142.76, 142,68, 142.29, 142.13, 142.07, 141.86, 141.82, 140.27, 139.69, 137.44, 134.19, 71.27 (2C, sp^3), 70.20 (2CH), 52.95 (OMe), 52.49 (OMe), 52.11 (OMe), 49.98 (CH_2), 47.80 (CH_2), 34.36 (CH_2), 32.64 (CH_2), 29.30 (CH_2), 29.24 (CH_2), 29.18 (CH_2), 29.08 (CH_2), 25.00 (CH_2), 24.78 (CH_2). FT-IR (microscope): 1750, 1679, 1656 cm^{-1}. MALDITOF-MS: *m*/*z* (rel intens) 1229 (100, $M^+ + Na$), 880 (16), 820 (15), 720 (12, C_{60}^+). UV−vis: 257, 314, 431 nm. Anal. Calcd for $C_{82}H_{34}O_{10}N_2$: C, 81.59; H, 2.84; N, 2.32. Found: C, 81.58; H, 2.54; N, 2.15.

Aza-18-crown-6 Amide of the Sebacoyl-2,5-dimethoxycarbonyl[60]fulleropyrrolidine (16). Procedure 1: Sebacoyl chloride (250 mg, 1.05 mmol), compound **1** (57 mg, 0.065 mmol), and pyridine (2 mL) in toluene (80 mL) were mixed and stirred for 24 h, then aza-18-crown-6 (450 mg, 1.71 mmol) was added, and the resulting solution was stirred for 3 d, treated as in the preparation general procedure (70 mg, 83% yield). Procedure 2: To a stirred solution of **4** (80 mg, 0.075 mmol) in freshly distilled chloroform (60 mL) were added aza-18-crown-6 (59 mg, 0.226 mmol), BtOH (61 mg, 0.452 mmol), and DCC (93 mg, 0.452 mmol) under nitrogen. The reaction mixture was stirred at rt for 48 h. The solvent was evaporated. The brown residue was extracted with toluene and chromatographed on a silica gel column (about 8 cm high and 2.5 cm in diameter). Chloroform first eluted some unreacted **4** (less than 10 mg) and then eluted the product **16**. The solvent chloroform was evaporated. The residue was treated with methanol and petroleum ether (bp 30−60 °C) and then dried under vacuum to give **16** as a brown powder (79 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.3−1.4 (m, 6H), 1.4−1.43 (m, 2H), 1.5−1.53 (m, 2H), 1.8−1.9 (m, 2H), 2.36 (t, 2H, J = 7.2 Hz), 2.82 (t, 2H, J = 7.2 Hz), 3.6−3.7 (m, 24H), 3.95 (s, 6H), 6.58 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.39 (CO), 172.49 (CO), 169.05 (CO), 153.62, 150.25, 147.56, 146.46, 146.42, 146.21, 146.15, 145.81, 145.68, 145.61, 145.57, 145.54, 145.42, 145.37, 144.52, 144.47, 144.32, 143.25, 143.18, 142.80, 142.72, 142.33, 142.15, 142.11, 141.80, 141.86, 140.26, 139.67, 137.48, 134.16, 71.19 (2C, sp^3), 70.89 (2CH), 70.86 (CH_2), 70.84 (CH_2), 70.81 (CH_2), 70.73 (CH_2), 70.70 (CH_2), 70.61 (CH), 70.39 (CH_2), 70.24 (CH_2), 70.11 (CH_2), 69.60 (CH_2), 52.99 (OMe), 48.97 (CH_2), 46.88 (CH_2), 34.41 (CH_2), 33.15 (CH_2), 29.51 (CH_2), 29.45 (CH_2), 29.40 (CH_2), 29.31 (CH_2), 25.34 (CH_2), 25.07 (CH_2). FT-IR (microscope): 1749, 1681, 1633 cm^{-1}. MALDITOF-MS: *m*/*z* (rel intens) 1309 (100, $M^+ + 1$), 720 (15, C_{60}^+). UV−vis: 256, 314, 431 nm. Anal. Calcd for $C_{88}H_{48}O_{11}N_2 \cdot C_7H_8 \cdot 2H_2O$: C, 79.38; H, 4.21; N, 1.95. Found: C, 79.34; H, 4.13; N, 1.82.

Sebacoyl-Bridged Bis(2,5-dimethoxycarbonyl[60]-fulleropyrrolidine) (17). To a stirred solution of **4** (57 mg, 0.054 mmol) in freshly distilled chloroform (80 mL) were added compound **1** (95 mg, 0.11 mmol), BtOH (73 mg, 0.54 mmol), and DCC (111 mg, 0.54 mmol) under nitrogen. The reaction mixture was stirred at rt for 7 d in the dark. The product was purified as in procedure 2 of the synthesis of **16** (29 mg, 28% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.40−1.65 (m, 8H), 1.80−2.00 (m, 4H), 2.83 (t, 4H, J = 7.6 Hz), 3.95 (s, 12H), 6.58 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.45, 169.04, 153.63, 150.22, 147.57, 146.48, 146.43, 146.21, 146.16, 145.79, 145.69, 145.58 (br), 145.55, 145.42, 145.38, 144.52, 144.47, 144.33, 143.27, 143.20, 142.81, 142.74, 142.34, 142.13, 142.09, 141.90, 141.88, 141.85, 140.26, 139.70, 137.49, 134.14, 71.11, 70.25, 53.01, 34.34, 29.42, 29.23, 25.11. MS (MALDI-TOF): *m*/*z* (rel intens) 1963 (3, $M^+ + K$), 1947 (16, $M^+ + Na$), 880 (10), 820 (37), 720 (100, C_{60}^+). Anal. Calcd for $C_{142}H_{32}O_{10}N_2 \cdot H_2O$: C, 87.73; H, 1.76; N, 1.44. Found: C, 87.59; H, 1.65; N, 1.37.

1,10-Diaza-18-crown-6-Bridged Bis(sebacoyl-2,5-dimethoxycarbonyl[60]fulleropyrrolidine) (18). To a stirred solution of **4** (250 mg, 0.23 mmol) in freshly distilled chloroform (100 mL) were added 1,10-diaza-18-crown-6 (20 mg, 0.076 mmol), BtOH (95 mg, 0.7 mmol), and DCC (145 mg, 0.7 mmol) under nitrogen. The reaction mixture was stirred at rt for 11 d in the dark. The product was purified as in procedure 2 of the synthesis of **16** (37 mg, 21% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30−1.48 (m, 12H), 1.50−1.58 (m, 4H), 1.60−1.70 (m, 4H), 1.78−2.00 (m, 4H), 2.33 (t, 4H, J = 7.2 Hz), 2.82 (t, 4H, J = 7.2 Hz), 3.58−3.67 (m, 24H), 3.95 (s, 12H), 6.58 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.25, 172.47, 169.05, 153.56, 150.19, 147.53, 146.43, 146.39, 146.17, 146.12, 145.76, 145.65, 145.57, 145.54, 145.51, 145.38, 145.33, 144.48, 144.43, 144.29, 143.22, 143.14, 142.76, 142.69, 142.29, 142.11, 142.08, 141.85 (br), 141.82, 140.22, 139.65, 137.44, 134.13, 70.90, 70.76, 70.53, 70.41, 70.17, 70.06, 70.01, 69.57, 53.01, 34.38, 33.15, 29.48, 29.42, 29.39, 29.28, 25.32, 25.04. MS (MALDI-TOF): *m*/*z* (rel intens) 2392 (9, $M^+ + K$), 2376 (39, $M^+ + Na$), 2354 (55, $M^+ + 1$), 1475 (100), 1309 (36). Anal. Calcd for $C_{164}H_{72}O_{16}N_4 \cdot BtOH \cdot 2H_2O$: C, 80.85; H, 3.23; N, 3.88. Found: C, 79.96; H, 3.14; N, 4.09.

Piperazine-Bridged Bis(sebacoyl-2,5-dimethoxycarbonyl[60]fulleropyrrolidine) (19). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.40−1.91 (m, 24H), 2.35 (t, 4H, J = 7.2 Hz), 2.82 (t, 4H, J = 7.2 Hz), 3.4−3.5 (m, 4H), 3.6−3.66 (m, 4H), 3.95 (s, 12H), 6.57 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.45 (2CO), 169.02 (2CO), 153.57, 150.17, 147.53, 146.44, 146.39, 146.18, 146.13, 145.75, 145.65, 145.56, 145.54, 145.52, 145.39, 145.34, 144.48, 144.43, 144.28, 143.23, 143.15, 142.77, 142.70, 142.30, 142.11, 142.08, 141.86, 141.84, 140.23, 139.65, 137.44, 134.11, 70.35 (2CH), 52.97 (OMe), 34.35 (CH_2), 33.15 (CH_2), 29.67 (CH_2), 29.37 (CH_2), 29.27 (CH_2), 2 9.20 (CH_2), 26.39 (CH_2),

26.30 (CH_2), 25.32 (CH_2), 25.07 (CH_2). FT-IR (microscope): 1745, 1667 cm^{-1}. MALDITOF-MS: *m/z* (rel intens) 2200 (78, $M^+ + 1 + Na$), 880 (15), 820 (61), 720 (100, C_{60}^+). UV−vis: 256, 314, 431 nm. Anal. Calcd for $C_{156}H_{56}O_{12}N_4 \cdot 4H_2O$: C, 83.27; H, 2.87; N, 2.49. Found: C, 83.10; H, 2.79; N, 2.12.

2-Hydroxyethanol-Bridged Bis(sebacoyl-2,5-dimethoxycarbonyl[60]fulleropyrrolidine) (20). ^1H NMR (400 MHz, $CDCl_3$): δ 1.32−1.49 (m, 12H), 1.49−1.54 (m, 4H), 1.54−1.70 (m, 4H), 1.90−2.00 (m, 4H), 2.34 (t, 4H, $J = 7.2$ Hz), 2.82 (t, 4H, $J = 7.2$ Hz), 3.95 (s, 12H), 4.28 (s, 4H), 6.58 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.50, 172.43, 169.03, 153.60, 150.21, 147.55, 146.45, 146.41, 146.19, 146.14, 145.77, 145.67, 145.58, 145.55, 145.53, 145.40, 145.35, 144.50, 144.45, 144.31, 143.24, 143.17, 142.78, 142.71, 142.31, 142.13, 142.10, 141.88 (br), 141.84, 140.24, 139.67, 137.45, 134.15, 71.36, 70.22, 62.02, 52.99, 34.38, 34.12, 29.36, 29.28, 29.19, 29.10, 25.03, 24.88. MS (MALDI-TOF): *m/z* (rel intens) 2191 (32, $M^+ + K$), 2175 (100, $M^+ + Na$), 2153 (25, M^+). Anal. Calcd for $C_{154}H_{52}O_{14}N_2 \cdot 2H_2O$: C, 84.46; H, 2.58; N, 1.28. Found: C, 84.48; H, 2.74; N, 1.31.

Tris(2-aminoethyl)amine-Linked Tris(sebacoyl-2,5-dimethoxycarbonyl[60]fulleropyrrolidine) (21). To a stirred solution of **4** (300 mg, 0.28 mmol) in freshly distilled chloroform (80 mL) were added tris(2-aminoethyl)amine (11.8 mg, 0. 079 mmol), BtOH (114 mg, 0.84 mmol), and DCC (174 mg, 0.85 mmol) under nitrogen. The reaction mixture was stirred at rt for 20 d in the dark. The product was purified as in procedure 2 of the synthesis of **16** (78 mg, 30% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 1.35−1.52 (m, 30H), 1.85−1.95 (m, 6H), 2.24 (t, 6H, $J = 7.2$ Hz), 2.56 (br, 6H), 2.82 (t, 6H, $J = 7.2$ Hz), 3.29 (br, 6H), 3.94 (s, 18H), 6.59 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.68, 172.40, 168.92, 153.47, 150.08, 147.42, 146.33, 146.27, 146.06, 146.01, 145.64, 145.54, 145.42 (br), 145.26, 145.23, 144.37, 144.32, 144.20, 143.11, 143.03, 142.66, 142.58, 142.18, 142.00, 141.96, 141.75 (br), 141.70, 140.10, 139.53, 137.30, 134.01. DEPT 135 NMR: δ 70.22 (CH), 54.58 (CH_2), 53.02 (CH_3), 37.68 (CH_2), 36.56 (CH_2), 34.38 (CH_2), 29.46 (CH_2), 29.42 (CH_2), 29.36 (CH_2), 29.31 (CH_2), 25.83 (CH_2), 25.62 (CH_2). MS (MALDI-TOF): *m/z* (rel intens) 3321 (14, $M^+ + K$ requires 3320), 2753 (14), 720 (100, C_{60}^+). Anal. Calcd for $C_{234}H_{87}O_{18}N_7 \cdot 2H_2O$: C, 84.65; H, 2.76; N, 2.95. Found: C, 84.48; H, 2.63; N, 2.82.

1,4,8,11-Tetraaza-14-crown-4-Linked Tetrakis(sebacoyl-2,5-dimethoxycarbonyl[60]fulleropyrrolidine) (22). To a stirred solution of **4** (400 mg, 0.38 mmol) in freshly distilled chloroform (100 mL) were added 1,4,8,11-tetraaza-14-crown-4 (15 mg, 0.075 mmol), BtOH (127 mg, 0.94 mmol), and DCC (193 mg, 0.94 mmol) under nitrogen. The reaction mixture was stirred at rt for 20 d in the dark. The product was purified as in procedure 2 of the synthesis of **16** (69 mg, 21% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 1.30−1.60 (m, 36H), 1.60−2.00 (m, 16H), 2.31 (t, 4H, $J = 7.0$ Hz), 2.41 (t, 4H, $J = 7.0$ Hz), 2.82 (t, 8H, $J = 7.0$ Hz), 3.30−3.65 (m, 16H), 3.95 (s, 24H), 6.57 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.50, 169.06, 153.65, 150.29, 147.57, 146.49, 146.42, 146.22, 146.16, 145.82, 145.76, 145.69, 145.59, 145.56, 145.42, 145.39, 144.53, 144.48, 144.36, 143.27, 143.18, 142.81, 142.74, 142.35, 142.15, 142.14, 141.91 (br), 141.85, 140.26, 139.69, 137.49, 134.18. DEPT 135 NMR: δ 70.22 (CH), 53.04 (CH_3), 47.42 (CH_2), 45.51 (CH_2), 34.42 (CH_2), 33.42 (CH_2), 32.85 (CH_2), 29.46 (br, CH_2), 25.55 (CH_2), 25.13 (CH_2). MS (MALDI-TOF): *m/z* (rel intens) 4421 (65, $M^+ + K$), 4405 (100, $M^+ + Na$), 3573 (25), 2482 (82). Anal. Calcd for $C_{314}H_{116}O_{24}N_8 \cdot CHCl_3 \cdot 3H_2O$: C, 83.03; H, 2.72; N, 2.46. Found: C, 82.96; H, 2.86; N, 2.61.

1,2,3,4,5,6-Hexakis(aminoethylsulfanylmethyl)benzene-Linked Hexakis(sebacoyl-2,5-dimethoxycarbonyl[60]-fulleropyrrolidine) (23). To a stirred solution of **4** (300 mg, 0.28 mmol) in freshly distilled chloroform (100 mL) were added 1,2,3,4,5,6-hexakis(aminoethylsulfanylmethyl)benzene (17 mg, 0.028 mmol), BtOH (95 mg, 0.69 mmol), and DCC (145 mg, 0.70 mmol) under nitrogen. The reaction mixture was stirred at rt for 35 d in the dark. The product was purified as in procedure 2 of the synthesis of **16** (50 mg, 26% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 1.35−1.70 (m, 60H), 1.82−1.95 (m, 12H), 2.15−2.35 (m, 12H), 2.81 (br t, 12H), 3.35−3.65 (br, 12H), 3.65−3.82 (br, 12H), 3.94 (s, 36H), 4.00−4.30 (br, 12H), 6.59 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 158.36, 147.57, 146.49, 146.42, 146.22, 146.17, 145.69, 145.56, 145.42, 145.38, 145.22, 144.52, 144.35, 143.26, 142.81, 142.75, 142.33, 142.15, 141.91, 141.88, 141.85, 140.26, 139.69, 137.45 (other signals are too weak and cannot be assigned unambiguously). DEPT 135 NMR: δ 70.30 (CH), 58.50 (CH_2), 53.04 (CH_3), 34.39 (CH_2, br), 29.29 (CH_2, br), 25.05 (CH_2, br). MS (MALDI-TOF): *m/z* (rel intens) 4935 (40, $M - 2 \times$ **1** $- OC(CH_2)_8CO - CO$ requires 4930), 3810 (70), 2686 (100). Anal. Calcd for $C_{480}H_{186}O_{36}N_{12}S_6 \cdot 2CHCl_3$: C, 81.25; H, 2.66; N, 2.36. Found: C, 81.30; H, 2.77; N, 2.31.

2,5-*trans*-Dimethoxycarbonylfulleropyrrolidine (24). Glycine methyl ester hydrochloride (40 mg, 0.32 mmol) was dissolved in 0.5 mL of water and then diluted with 20 mL of methanol. The resulting solution was added to a C_{60} (60 mg, 0.083 mmol)/toluene (250 mL) solution. After methyl glyoxylate (12 mg, 0.14 mmol) was added, the solution was refluxed for periods of 6, 18, and 24 h, respectively, for three independent runs. The solution was evaporated, and the residue was chromatographed on silica gel. Toluene first eluted some unreacted C_{60}, followed by the product bands. ^1H NMR (400 Hz, $CDCl_3$): δ 3.90 (s, 6H), 4.24 (t, 1H, $J = 8.8$ Hz), 6.06 (d, 2H, $J = 8.8$ Hz). ^{13}CNMR (100 MHz, $CDCl_3$): δ 170.93 (CO), 153.71, 150.49, 147.23, 146.40, 146.35, 146.07, 145.62, 145.51, 145.46, 145.38, 145.35, 144.49, 144.29, 143.14, 142.74, 142.23 (br), 141.89, 140.13 (br), 139.80, 136.51, 135.62, 73.84, 52.69 (OMe). FT-IR (microscope): 1748, 1678 cm^{-1}. UV−vis: 256, 314, 430 nm.

Monoacylated Sebacoyl Derivative of 2,5-trans-Dimethoxycarbonylfulleropyrrolidine (25). The procedure is similar to that of the preparation of **4**. UV−vis: 256, 314, 413 nm. ^1H NMR (400 MHz, $CDCl_3$ 298 K): δ 1.30−1.80 (m, 10H), 1.80−2.00 (m, 2H), 2.39 (t, 2H, $J = 7.2$ Hz), 2.47−2.55 (m, 1H), 2.69−2.77 (m, 1H), 3.85 (s, 3H), 3.96 (s, 3H), 6.42 (s, 2H). ^1H NMR (400 MHz, $CDCl_3$ 323 K): δ 1.30−1.80 (m, 10H), 1.80−2.00 (m, 2H), 2.39 (t, 2H, $J = 7.2$ Hz), 2.47−2.55 (m, 1H), 2.69−2.77 (m, 1H), 3.87 (s, 6H), 6.42 (s, 2H).

HPLC Separation Experiments. A (*S*)-*tert*-leucine-based chiral analytical column (250 × 4.6 mm) from Phenomenex was eluted with a mixture of chloroform and petroleum ether (bp 60−90 °C). For analysis purposes the ratio of the solvents was 20:80 between chloroform and petroleum ether. At a flow rate of 1 mL/min, the retention times were 15.1 min for **1**, 17.6 min for (*R*)-**24**, and 18.5 min for (*S*)-**24** as determined from a mixture of **1** and **24**, the ratio of which was 0.66:1.05 from ^1H NMR and 0.65:1.10 from HPLC integrals. Both the retention time and integral of the peaks were the same when the detector wavelength was set at 254 and 430 nm. For collection of the individual peaks of the enantiomeric **24** the ratio of chloroform and petroleum ether was changed to 10:90 to get better separation. With this ratio and at a flow rate of 1 mL/min, the retention times were 50.5 min for (*R*)-**24** and 55.7 min for (*S*)-**24**. The sample (20 μL for each run) was injected directly as a $CDCl_3$ solution (after NMR measurement).

CD Spectrum Measurement. The spectra were obtained on a JASCO J-715 spectropolarimeter at rt in chloroform solution.

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Supporting Information Available: Representative copies of ^1H and ^{13}C NMR and MS spectra for the new compounds and details of the synthesis of compounds **8**−**15**, **19**, and **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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