Synthesis and Solubility Properties of Methanofullerenes Containing Primary Ammonium Ion Functionalities

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The synthesis of novel methanofullerene derivatives bearing a primary ammonium ion functionality is described. They are obtained by a Bingel cyclopropanation reaction on C_{60} with malonate esters, bearing both a solubilizing poly(oxyethylene) chain and an aliphatic chain ending with a BOC-protected amine. After removal of the protecting group, a counterion exchange methodology allows for the introduction of a perfluorinated anion, bringing the overall solubility of these derivatives to 98 mg/mL in an organic CH_2Cl_2 solution.

Introduction

C_{60} fullerenes, in combination with conducting polymers, are amongst the most popular building blocks that synthetic organic chemists are currently exploiting in an attempt to prepare efficient organic solar cells.[1] The peculiar properties of fullerene as an electron acceptor have been studied in detail in molecular dyads, in which electron transfer can be photoinduced from a donor (D) subunit to an acceptor (A) C_{60} unit. A charge-separated complex is generated, which, if stable enough, can produce a photocurrent.[2] Fullerene-containing polymers are known but their use so far has been hampered not only because of the problems associated with their synthesis but also because of their low solubility in common organic solvents.[3] In the preparation of solar-cell functional devices, the possibility of anchoring, in a covalent way, the photoactive C_{60} units to the polymeric donor substrate, has been explored and recently reviewed.[4] Noncovalent bonds have intrinsic features that can be useful in the material properties of functional devices,[5] and several research groups have reported studies of supramolecular dyads in solution.[6,7]

The solubility of the compounds used in devices is actually an important factor in the preparation of thin polymeric films of different thicknesses; blends of compounds and polymers with very different solubility characteristics tend to crash out or to phase-segregate during deposition when techniques such as spin coating are used. On the other hand, fullerene derivatives with hydrophilic groups of both ionic and non-ionic nature have been reported to organize in supramolecular structures with sizes that range from nanometer to micrometer in length.[8] In other reports, fullerene derivatives containing one or two primary ammonium ion functionalities have been reported,[9] and used, as their chloride salts, in H_2O solutions for enzyme inhibition.[10]

In this paper, we describe our strategy and synthetic efforts to achieve C_{60} derivatives that contain *one* primary ammonium ion functionality and that are highly soluble in common organic solvents. Solubility in apolar organic solvents that do not compete for hydrogen bonds is necessary to allow the primary ammonium ion functionality to recognize suitable guests such as crown ethers that are possibly positioned on macromolecular substrates in functional devices.

Results and Discussion

Given the liphophilicity of the fullerene core (C_{60} itself is only sparingly soluble in aromatic solvents such as toluene) and the hydrophilicity of a primary ammonium ion functionality, the introduction of a) a solubilizing chain, and b) a liphophilic counterion, was deemed necessary for our purpose. Furthermore, because of the high reactivity of amines towards the C_{60} scaffold, an acid-labile protecting group for the amino group should be used in order to obtain an ammonium ion directly during the final deprotection step. In our first approach to tackle this problem, we treated *N*-protected amino alcohol **2a**[11] with commercially available ethyl malonyl chloride (**1**) to give malonate derivative **3** in good yields (Scheme 1). As mentioned above, in our design scheme, the second malonate "arm" also had to be functionalized with a more powerful solubilizing chain.

It is well known that methanofullerenes comprising a closed crown ether or an open ethylene glycol structure are highly soluble in organic chlorinated solvents.[12] We therefore synthesized derivatives **5**–**7** by functionalization of the

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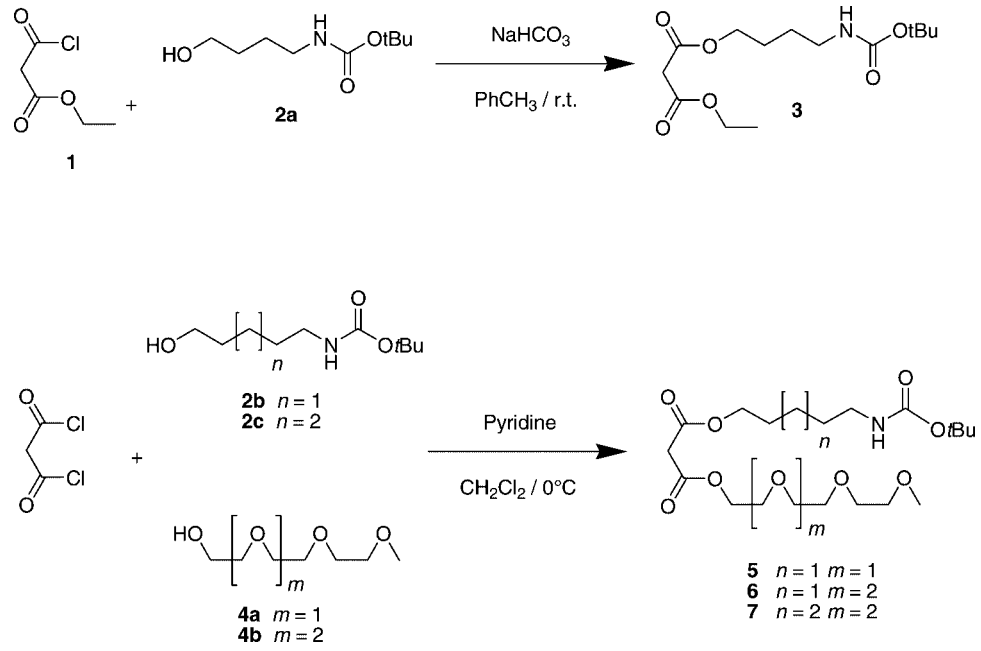


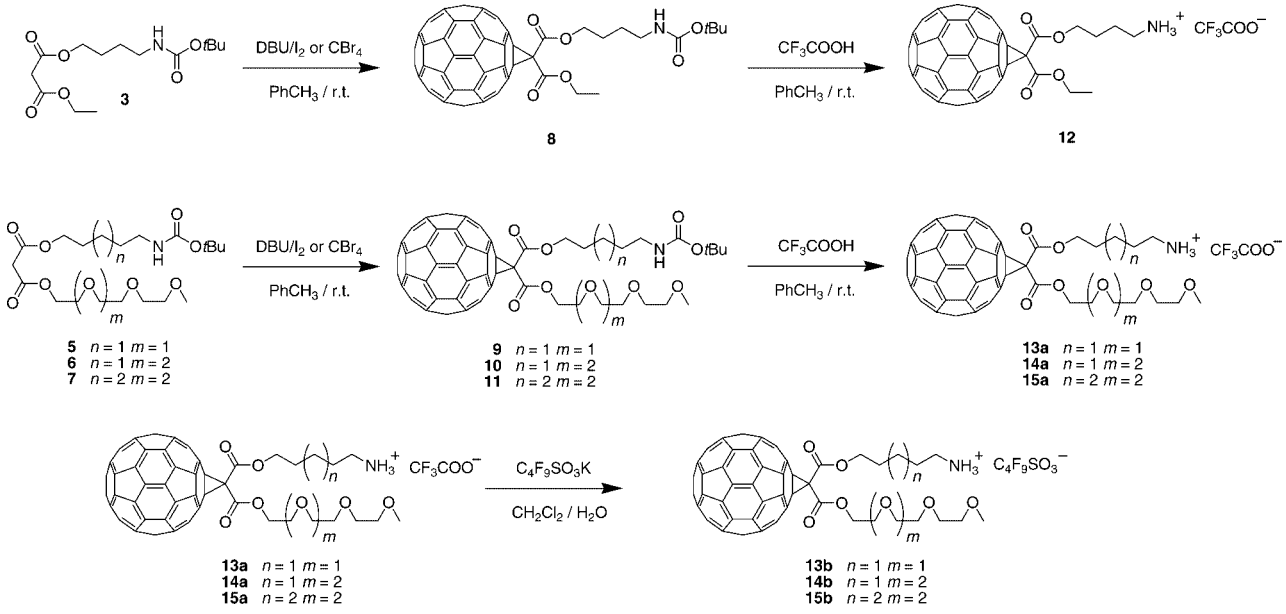
Scheme 1. Preparation of malonate derivatives **3**, **5**, **6**, and **7**.

two malonate "arms" with both an *N*-protected amino alcohol with an increasing number of carbon atoms (**2b**[13] and **2c**[14]), and monomethyl ether oligoethylene glycols **4a** and **4b**. Reaction of malonyl dichloride with one equivalent each of amino alcohols **2** and oligoethylene glycol derivatives **4** gave derivatives **5**–**7** in statistical yields (30–40%). The products were purified by column chromatography and easily separated from the homocoupled malonate products, and contained either only *N*-protected amino alcohol or only ethylene glycol derivatives.

The synthesis of methanofullerenes **8**–**11** is shown in Scheme 2. The yields, after purification, were in the 35–40% range; they are satisfactory in view of the ability of C_{60} to undergo multiple addition in the Bingel cyclopropanation reaction.[15] Removal of the amino protecting-group was carried out with trifluoroacetic acid in toluene to give the corresponding salts in near quantitative yields.

The solubility issues highlighted in the introduction were most evident for derivative **12**, which was only sparingly soluble in $CDCl_3$, and for which a good quality ^1H NMR spectrum could not be obtained.

The solubilities of compounds **13a**–**15a**, as judged qualitatively, were considerably higher. In order to reduce the polarity of the polar ammonium salt functionality, we chose the use of a very liphophilic perfluorinated counterion. This counterion has previously been used, for example, in combi-



Scheme 2. Synthesis of fullerene salts **12**–**15**.

nation with aromatic sulfonium cations in microlithography applications.[16] The counterion exchange was performed by shaking a CH_2Cl_2 solution of the fullerene derivative as the trifluoroacetate salt and a H_2O solution of the commercially available potassium nonafluorobutane sulfonate. The organic layer contained the newly formed, more soluble salt. After drying, compounds **13b**–**15b** were obtained as brown solids and were characterized by elemental analyses.

The ability of the fullerene-containing ammonium salt to bind 18-crown-6, as known for primary ammonium ion derivatives, was tested by ESI mass spectroscopy. Even in the presence of 50% v/v of a solvent that competes for the hydrogen bonding, such as MeOH, 1:1 complex formation in the gas phase was clearly detected (see Figure 1).

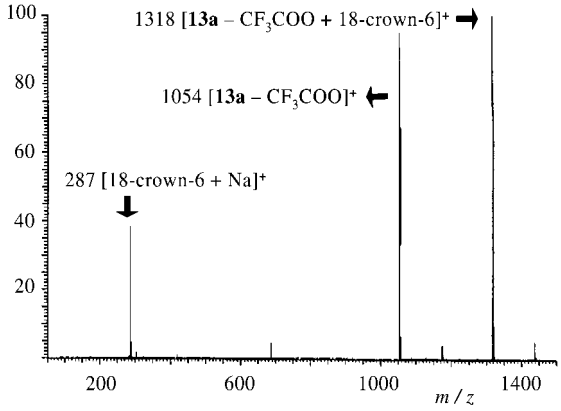


Figure 1. Mass spectrum (ESI) of a 1:1 solution of **13a** and 18-crown-6 in $CHCl_3$:MeOH (1:1).

Furthermore, evidence for the formation, in the gas phase, of a fullerene dimer was obtained by analyzing a 1:1 solution of compound **13a** and a fullerene compound containing a 18-crown-6 derivative, which was previously synthesized by us and whose binding ability towards a primary ammonium ion was demonstrated (see Supporting Information).[12c]

The solubilities of the compounds in CH_2Cl_2 were determined at room temperature, and the values are reported in Table 1.

Table 1. Solubilities in CH_2Cl_2 at room temperature for the salts synthesized in this work.

Entry	Compound	Solubility [mg/mL]	Solubility [mol/L]
1	**13a**	3	2.6×10^{-3}
2	**14a**	26	2.2×10^{-2}
3	**15a**	33	2.7×10^{-2}
4	**13b**	18	1.3×10^{-2}
5	**14b**	60	4.3×10^{-2}
6	**15b**	98	7.0×10^{-2}

It is evident that the oxyethylene chain has a beneficial effect in solubilizing the ammonium ion functionality, since the solubility is nine times higher when an additional oxyethylene unit is inserted in the solubilizing spacer (entries 1 versus 2 in Table 1).

The addition of an extra carbon atom in the spacer group instead has a minimal beneficial effect (entries 2 versus 3). The introduction of the nonafluorobutane sulfonate counterion has a dramatic effect on the solubilities of these salts. The values in entries 4, 5, 6 are between 2 and 5 times higher (considering molar solubilities) than those of the corresponding trifluoroacetate salts **13a**–**15a**.

Conclusions

By judicious choice of the solubilizing group and of the counterion it is possible to obtain fullerene salts containing a primary ammonium functionality with solubilities of up to 98 mg/mL (0.07 M) in CH_2Cl_2. Their ability to form complexes with 18-crown-6 and supramolecular dimers with fullerene-containing crown ethers has been demonstrated in the gas phase. The presence of a functional group that is able to be "anchored" in a noncovalent fashion to crown ether derivatives and/or to appropriately functionalized conducting polymers[17] is promising for the possible inclusion of these compounds in thin films for photovoltaic applications.

Experimental Section

General: All commercially available compounds were purchased from Aldrich and used as received. THF (CaH_2) and CH_2Cl_2 (CaH_2) were dried and distilled before use. Compounds *N*-*tert*-butoxycarbonyl-4-aminobutanol (**2a**),[11] *N*-*tert*-butoxycarbonyl-5-aminopentanol (**2b**),[13] *N*-*tert*-butoxycarbonyl-6-aminohexanol (**2c**),[14] and fullerene derivative **16**[12c] were prepared according to literature procedures. ^1H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on Bruker 200 or AMX300 with the solvent residual proton signal or tetramethylsilane (TMS) as a standard. Infrared spectra were recorded with Perkin–Elmer 881 using NaCl or KBr disks. Mass spectra were recorded using an Electrospray Ionization instrument LCQ Decca (Thermofinnigan). Melting points were recorded on a Büchi 510 apparatus and are uncorrected.

Compound 3: Ethyl malonyl chloride **1** (398 mg, 2.64 mmol) in dry toluene (5 mL) was slowly added at room temperature to a solution of **2a** (0.5 g, 2.64 mmol) and excess solid $NaHCO_3$ in toluene (50 mL). The mixture was stirred overnight at room temperature. The mixture was filtered, washed with brine, and dried (Na_2SO_4), and the solvent removed in vacuo. The residue was purified by column chromatography (SiO_2; hexanes/AcOEt, 6:4) to give **3** as a colorless oil (530 mg, 66%). IR (NaCl) $\tilde{\nu}$ = 3500, 2990, 1725, 1350, 1220 cm^{-1}. ^{1}HNMR (300 MHz, $CDCl_3$): δ = 1.27 (m, 3 H, $-CH_2CH_3$), 1.42 (s, 9 H, *tert*-butyl), 1.60 (m, 4 H, CH_2), 3.12 (m, 2 H, $-CH_2NH$), 3.35 (s, 2 H, $-COCH_2CO-$), 4.16 (m, 4 H, $-CH_2OCO-$ and CH_3CH_2O-), 4.73 (br. s, 1 H, –NH) ppm. ^{13}CNMR (75 MHz, $CDCl_3$): δ = 14.42, 26.17, 26.93, 28.76, 40.45, 41.97, 61.89, 65.47, 79.5, 156.35, 166.95 ppm.

General Procedure for the Preparation of Mixed Malonic Esters 5–7: Malonyl dichloride (0.99 mmol) in CH_2Cl_2 (5 mL) was added dropwise at 0 °C to a solution of the appropriate (*tert*-butoxycarbonyl)amino alcohol (0.99 mmol), oligoethyleneglycol monomethyl

ether (0.99 mmol), and pyridine (0.16 mL, 1.98 mmol) in CH_2Cl_2 (200 mL). The mixture was left at 0 °C for 30 min, stirred overnight at room temperature, then washed with a saturated NH_4Cl solution, and dried (Na_2SO_4), and the solvent was removed in vacuo.

Compound 5: Prepared from malonyl dichloride (139 mg, 0.99 mmol), **2b** (200 mg, 0.99 mmol), and triethyleneglycol monomethyl ether **4a** (162 mg, 0.99 mmol). The product was purified by column chromatography (SiO_2; hexanes/AcOEt 30–100%) to give **5** as a colorless oil (160 mg, 37%). IR (NaCl) $\tilde{\nu}$ = 3364, 2933, 1710, 1732, 1250 cm^{-1}. ^{1}HNMR (300 MHz, $CDCl_3$): δ = 1.44 (s, 9 H, *tert*-butyl), 1.50 (m, 6 H, CH_2), 3.11 (m, 2 H, –CH_2NH–), 3.39 (s, 2 H, –CH_2COO–), 3.39 (s, 3 H, CH_3OCH$_2$–) 3.55 (m, 2 H, –CH_2OCH$_3$), 3.64 (m, 6 H, –CH_2O–), 3.71 (m, 2 H, –OCH_2CH$_2$-OCO–), 4.14 (m, 2 H, –CH$_2$CH_2OCO–), 4.30 (m, 2 H, –OCH$_2$-CH_2OCO–), 4.59 (br. s, 1 H, –N*H*) ppm. ^{13}CNMR (75 MHz, $CDCl_3$): δ = 22.84, 27.9, 28.22, 29.43, 40.16, 41.22, 58.82, 65.16, 68.65, 70.38, 71.72, 78.86, 155.8, 166.28, 166.42 ppm. ESI-MS: *m*/*z* (%) = 458 (100) [*M* + Na]$^+$.

Compound 6: Prepared from malonyl dichloride (1 g, 7.4 mmol), **2b** (1.5 g, 7.4 mmol), and tetraethyleneglycol monomethyl ether **4b** (1.5 g, 7.4 mmol). The product was purified by column chromatography (SiO_2; hexanes/AcOEt 30–100%) to give **6** as a colorless oil (1.28 g, 36%). IR (NaCl) $\tilde{\nu}$ = 3361, 2931, 1734, 1713, 1521, 1456, 1248, 1143 cm^{-1}. ^{1}H NMR: (300 MHz, $CDCl_3$): δ = 1.44 (s, 9 H, *tert*-butyl), 1.55 (m, 6 H, CH_2), 3.11 (m, 2 H, –CH_2NH–), 3.42 (s, 2 H, –CH_2COO–), 3.39 (s, 3 H, CH_3OCH$_2$–), 3.60 (m, 2 H, CH_2OCH$_3$), 3.64 (m, 6 H, –CH_2O), 3.77 (m, 2 H, –OCH_2-CH$_2$OCO–), 4.14 (m, 2 H, –CH$_2$CH_2OCO–), 4.26 (m, 2 H, –OCH$_2$-CH_2OCO–), 4.60 (br. s, 1 H, –N*H*) ppm. ^{13}CNMR (75 MHz, $CDCl_3$): δ = 22.92, 27.80, 27.98, 28.30, 28.97, 29.51, 40.21, 41.30, 59.91, 61.04, 62.10, 64.46, 65.24, 68.73, 69.53, 70.40, 70.47, 71.80, 78.95 ppm. ESI-MS: *m*/*z* (%) = 502 (100) [*M* + Na]$^+$.

Compound 7: Prepared from malonyl dichloride (320 mg, 2.3 mmol), **2c** (500 mg, 2.3 mmol), and tetraethyleneglycol monomethyl ether **4b** (478 mg, 2.3 mmol). The product was purified by column chromatography (SiO_2; hexanes/AcOEt 30–100%) to give **7** as a colorless oil (390 mg, 35%). IR (NaCl) $\tilde{\nu}$ = 3366, 2932, 1700, 1736, 1521, 1455, 1366, 1248, 1171, 1044, 854 cm^{-1}. ^{1}HNMR (300 MHz, $CDCl_3$): δ = 1.30–1.70 (m, 17 H, *tert*-butyl and aliphatic –CH$_2$–), 3.10 (br. s, 2 H, CH_2NH), 3.40 (s, 3 H, CH_3–O–CH$_2$–), 3.42 (s, 2 H, –CH$_2$–COO–), 3.55 (m, 2 H, –OCH$_2$–CH$_2$–O–), 3.67 (m, 10 H, –OCH$_2$–CH$_2$–O–), 3.70 (m, 2 H, –OCH$_2$CH$_2$O–), 4.15 (m, 2 H, –OCH$_2$CH$_2$O–), 4.30 (m, 2 H, –OCH$_2$CH$_2$O–), 4.55 (br. s, 1 H, NH) ppm.

General Procedure for the Preparation of Methanofullerenes 8–11: A solution of DBU (0.5 mmol) in toluene (5 mL) was added dropwise to a solution of the appropriate malonate derivative (**3**, **5**, **6**, or **7**) [0.2 mmol], C_{60} (0.2 mmol), and I_2 or CBr_4 (0.2 mmol) in toluene (130 mL). Stirring, under nitrogen, was continued for 12 h. The solution was washed once with water (50 mL) and dried (Na_2SO_4). The product were purified by column chromatography (SiO_2) by passing the toluene solution through the column to separate only the unreacted C_{60} − eluted with the front of the solvent − then shifting to toluene/*i*PrOH (98:2) to separate the methanofullerenes. The purified oily products were dissolved in a minimum amount of CH_2Cl_2 (ca. 5 mL), precipitated as dark amorphous powders by addition of larger amounts of MeOH (ca. 100 mL), and separated from the solvents by centrifugation. The final traces of the solvent were then removed in vacuo, and the solids finally dried under high vacuum for 3 h.

Compound 8: From compound **3** (300 mg, 1 mmol), C_{60} (720 mg, 1 mmol), CBr_4 (332 mg, 1 mmol), and DBU (334 mg, 2.2 mmol) to yield **8** as a dark solid (340 mg, 33%). M.p. >200 °C. IR (KBr) $\tilde{\nu}$ = 3417, 2927, 1745, 1234 cm^{-1}. ^{1}HNMR (300 MHz, $CDCl_3$): δ = 1.38 (m, 3 H, –CH$_2$CH_3), 1.62 (s, 9 H, *tert*-butyl), 1.84 (m, 4 H, aliphatic CH_2), 3.22 (m, 2 H, –CH_2NH–), 4.54 (5 H, m, –CH_2OCO–, –NH, and CH$_3$CH_2O–) ppm. ^{13}CNMR (75 MHz, $CDCl_3$): δ = 14.20, 25.84, 26.67, 28.34, 63.40, 66.81, 71.50, 138.83, 139.02, 140.87, 140.89, 141.8, 142.12, 142.9, 142.94, 143.01, 143.8, 144.54, 144.56, 144.61, 144.81, 145.06, 145.10, 145.15, 145.19, 145.23, 155.86, 163.48, 163.53 ppm.

Compound 9: From compound **5** (200 mg, 0.46 mmol), C_{60} (331 mg, 0.46 mmol), I_2 (117 mg, 0.46 mmol), and DBU (154 mg, 1 mmol) to yield **9** as a dark solid (150 mg, 38%). M.p. >200 °C. IR (KBr) $\tilde{\nu}$ = 3417, 2927, 1745, 1234 cm^{-1}. ^{1}HNMR (300 MHz, $CDCl_3$): δ = 1.51 (s, 9 H, *tert*-butyl), 1.89 (m, 6 H, aliphatic –CH$_2$–), 3.16 (m, 2 H, –CH_2NH–), 3.41 (s, 3 H, –OCH_3), 3.58 (m, 2 H, –CH_2OCH$_3$), 3.70 (m, 6 H, –CH_2O–), 3.90 (m, 2 H, –OCH_2CH$_2$OCO–), 4.53 (m, 2 H, –CH$_2$CH_2OCO–), 4.66 (m, 2 H, –OCH$_2$CH_2OCO–) ppm. ^{13}CNMR (75 MHz, $CDCl_3$): δ = 23.19, 28.15, 28.37, 29.61, 58.98, 66.15, 67.14, 68.72, 70.54, 70.56, 70.61, 71.43, 71.85, 138.88, 139.01, 140.84, 140.89, 141.80, 142.11, 142.93, 143.01, 143.81, 144.53, 144.61, 144.81, 145.07, 145.10, 145.13, 145.19, 155.88, 163.42, 163.56 ppm. ESI-MS *m*/*z* (%) = 1176 (100) [*M* + Na]$^+$.

Compound 10: From compound **6** (232 mg, 0.48 mmol), C_{60} (350 mg, 0.48 mmol), I_2 (122 mg, 0.48 mmol), and DBU (152 mg, 1.0 mmol) to yield **10** as a dark solid (119 mg, 20.7%). M.p. >200 °C. IR (KBr) $\tilde{\nu}$ = 3364, 2932, 1733, 1700, 1554, 1429, 1236, 1104 cm^{-1}. ^{1}HNMR (300 MHz, $CDCl_3$): δ = 1.45 (s, 9 H, *tert*-butyl), 1.56–1.9 (m, 6 H, aliphatic –CH$_2$–), 3.15 (br. s, 2 H, –CH_2NH–), 3.4 (s, 3 H, OCH$_3$), 3.6–3.7 (m, 12 H, –OCH$_2$CH$_2$O–), 3.9 (m, 2 H, –OCH$_2$CH$_2$O–), 4.5 (m, 2 H, –CH$_2$CH_2OCO–), 4.66 (m, 3 H, –OCH$_2$CH_2OCO– and –NH) ppm. ^{13}CNMR (75 MHz, $CDCl_3$): δ = 23.18, 28.12, 28.31, 28.36, 29.59, 40.31, 58.96, 66.08, 66.13, 67.14, 67.20, 68.65, 68.71, 69.33, 70.42, 70.50, 70.56, 71.40, 71.81, 79.02, 126.19, 127.76, 130.68, 130.77, 130.81, 132.70, 133.41, 133.45, 136.45, 136.86, 138.84, 139.00, 140.82, 140.87, 142.90, 142.92, 142.99, 143.77, 143.79 ppm. ESI-MS *m*/*z* (%) = 1220 (100) [*M* + Na]$^+$.

Compound 11: From compound **7** (300 mg, 0.61 mmol), C_{60} (500 mg, 0.61 mmol), I_2 (155 mg, 0.61 mmol), and DBU (230 mg, 1.52 mmol) to yield **11** as a dark solid (340 mg, 46%). M.p. >200 °C. IR (KBr) $\tilde{\nu}$ = 3404, 2926, 1745, 1700, 1454, 1366, 1251, 1109, 738, 699 cm^{-1}. ^{1}HNMR (300 MHz, $CDCl_3$): δ = 1.45 (s, 9 H, *tert*-butyl), 1.65–1.93 (m, 8 H, aliphatic –CH$_2$-), 3.05–3.2 (br. s, 2 H, –CH$_2$NH–), 3.4 (s, 3 H, –OCH$_3$–), 3.57 (m, 2 H, –OCH$_2$CH$_2$O–), 3.67 (m, 10 H, –OCH$_2$CH$_2$O–), 3.89 (m, 2 H, –OCH$_2$CH$_2$O–), 4.51 (m, 2 H, –OCH$_2$CH$_2$O–), 4.60 (br. s, 1 H, –NH–), 4.66 (m, 2 H, –OCH$_2$CH$_2$O–) ppm. ^{13}CNMR (75 MHz, $CDCl_3$): δ = 25.57, 26.29, 28.35, 29.95, 40.27, 52.11, 58.95, 66.10, 67.22, 67.29, 68.63, 68.68, 70.42, 70.49, 70.43, 70.59, 71.42, 71.82, 77.13, 79.03, 130.81, 130.84, 140.81, 140.85, 141.77, 142.09, 142.10, 142.87, 142.89, 142.91, 143.78, 143.79, 144.51, 144.58, 145.06, 145.14, 145.16, 145.23, 155.88, 163.41, 163.53 ppm. ESI-MS *m*/*z* (%) = 1112 (26) [M – BOC]$^+$, 1234 (100) [*M* + Na]$^+$.

General Procedure for the Preparation of Methanofullerene Ammonium Salts 12 and 13a–15a: The *N*-protected methanofullerene was dissolved in a 1:1 mixture of toluene/trifluoroacetic acid and left without stirring for 2–3 h. The reaction was monitored by TLC (SiO_2; toluene/propanol, 9:1). After completion of the deprotection, the solvents were evaporated, and some MeOH was added and evaporated again (2×). The residue was taken up in CH_2Cl_2, and the solution added dropwise to excess hexane. The precipitated

solid was separated by centrifugation, washed with a small amount of Et_2O, and then dried under high vacuum.

Compound 12: From compound **8** (40 mg, 0.04 mmol) to yield **12** as a dark brown solid (31 mg, 80%). M.p. >200 °C. IR (KBr) $\tilde{\nu}$ = 3417, 2927,1745, 1234 cm^{-1}. ^{1}HNMR (300 MHz, $CDCl_3$): the spectrum was of low quality but it shows the same signals as those for the C_{60} adduct of malonic acid 4-[(*tert*-butoxycarbonyl)amino] butyl ethyl ester – with the exception of the *tert*-butyl signals that are lacking.

Compound 13a: From compound **9** (35 mg, 0.03 mmol) to yield **13a** as a dark brown solid (28 mg, 80%). M.p. >200 °C. IR (KBr) $\tilde{\nu}$ = 3417, 1745 cm^{-1}. ^{1}HNMR (300 MHz, $CDCl_3$): δ = 1.89 (m, 6 H, aliphatic $-CH_2-$), 3.16 (m, 2 H, $-CH_2NH-$), 3.41 (s, 3 H, $-OCH_3$), 3.58 (m, 2 H, $-CH_2OCH_3$), 3.70 (m, 6 H, $-CH_2O-$), 3.90 (m, 2 H, $-OCH_2CH_2OCO-$), 4.53 (m, 2 H, $-CH_2CH_2OCO-$), 4.66 (m, 2 H, $-OCH_2CH_2OCO-$), 7.80 (br. s, 3 H, NH_3^+) ppm. ^{13}CNMR (75 MHz, $CDCl_3$): δ = 17.94, 18.45, 23.22, 26.80, 27.72, 29.6, 30.84, 33.86, 39.92, 58.83, 65.44, 66.81, 68.98, 69.87, 70.05, 70.2, 71.57, 102.75, 103.85, 138.88, 139.09, 140.89, 141.78, 142.11, 142.96, 143.8, 144.57, 144.88, 144.99, 145.12, 145.2, 163.38 ppm. ESI-MS *m*/*z* (%) = 1054 (100) $[M - CF_3COO]^+$.

Compound 14a: From compound **10** (80 mg, 0.067 mmol) to yield **14a** as a dark brown solid (68 mg, 93%). IR (KBr) $\tilde{\nu}$ = 3580, 1618, 1115 cm^{-1}. ^{1}HNMR (300 MHz, $CDCl_3$): δ = 1.66–1.95 (m, 6 H, aliphatic $-CH_2-$), 3.10 (m, 2 H, $-CH_2NH-$), 3.45 (s, 3 H, $-OCH_3$), 3.62 (m, 2 H, $-CH_2OCH_3$), 3.68 (m, 6 H, $-OCH_2CH_2O-$), 3.76 (m, 2 H, $-OCH_2CH_2O-$), 3.84 (m, 2 H, $-OCH_2CH_2OCO-$), 3.96 (m, 2 H, $-OCH_2CH_2OCO-$), 4.54 (m, 2 H, $-CH_2CH_2OCO-$), 4.67 (m, 2 H, $-OCH_2CH_2OCO-$), 7.80 (br. s, 3 H, NH_3^+) ppm. ESI-MS *m*/*z* (%) = 1098 (100) $[M - CF_3COO]^+$.

Compound 15a: From compound **11** (225 mg, 0.18 mmol) to yield **15a** as a dark brown solid (216 mg, 95%). M.p. >200 °C. IR (KBr) $\tilde{\nu}$ = 3445, 2916, 2863, 1743, 1683, 1229, 1202, 1128 cm^{-1}. ^{1}HNMR (300 MHz, $CDCl_3$): δ = 1.65–1.93 (m, 8 H, aliphatic $-CH_2-$), 3.05–3.20 (m, 2 H, $-CH_2NH-$), 3.50 (s, 3 H, $-OCH_3$), 3.54–4.6 (m, 14 H, $-OCH_2CH_2O-$), 4.54 (m, 2 H, $-CH_2CH_2OCO-$), 4.67 (m, 2 H, $-OCH_2CH_2OCO-$), 7.80 (br. s, 3 H, NH_3^+) ppm. ^{13}CNMR (75 MHz, $CDCl_3$): δ = 0.91, 25.09, 25.44, 28.06, 29.59, 32.34, 67.05, 69.34, 69.90, 70.13, 70.52, 70.69, 71.33, 71.41, 138.64, 139.32, 140.87, 141.77, 142.10, 142.86, 142.94, 143.77, 144.52, 144.59, 144.81, 145.09, 145.17 ppm. ESI-MS *m*/*z* (%) = 1112 (100) $[M - CF_3COO]^+$.

General Procedure for the Preparation of Nonafluorobutane Sulfonate Salts 13b–15b: The trifluoroacetate salt was dissolved in CH_2Cl_2 and washed three times with an aqueous 10^{-2} M solution of potassium nonafluorobutane sulfonate. The organic phase was dried (Na_2SO_4), and the solvents evaporated. The residue was taken up in CH_2Cl_2, and the solution added dropwise to excess hexane. The precipitated solid was separated by centrifugation, washed with a small amount of Et_2O, and then dried under high vacuum. The compounds were characterized by elemental analyses. **13b**, $C_{79}H_{28}O_{10}F_9NS$ (1353.8): calcd. C 70.06, H 2.07, N 1.0; found C 70.18, H 2.22, N 1.07. **14b**, $C_{81}H_{32}O_{11}NF_9S$ (1397.9): calcd. C 69.58, H 2.31, N 1.0; found C 70.05, H 2.58, N 1.04. **15b**, $C_{82}H_{34}O_{11}NF_9S$ (1411.9): calcd. C 69.7, H 2.41, N 1.0; found C 70.03, H 2.28, N 1.05.

General Procedure for the Determination of the Solubility of the Trifluoroacetate and Nonafluorobutane Sulfonate Salts: The trifluoroacetate (or nonafluorobutane sulfonate salt) was added to CH_2Cl_2 (1.5 mL) until some undissolved product was visible after stirring and ultrasonication for 30 s. The solution was centrifuged for 2 min, after which 1.3 mL of it was filtered through a small glass wool plug. Exactly 1 mL of this saturated solution was transferred into a small flask, evaporated, and the residue weighed.

Supporting Information: Mass spectrum (ESI) of a 1:1 solution of **13a** and a previously reported[12c] fullerene compound containing a 18-crown-6 derivative (see footnote on the first page of this article).

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