Novel Versatile Fullerene Synthons†

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We report the synthesis of three novel, versatile fullerene intermediates whose main feature is the presence of an amino end group. Simple condensation reactions of these intermediates under standard conditions produce new derivatives that are useful for applications in materials science and medicinal chemistry.

Introduction

The chemical modification of fullerenes has continued unabated in the past few years,[1,2] mainly devoted to the production of stable derivatives that are useful for applications in materials science[3,4] and medicinal chemistry.[5,6] C_{60} and its derivatives, in fact, have been considered for use in research fields currently of the highest technological interest because of several properties exhibited by this new allotropic form of carbon. It is the combination of these properties that makes these compounds so special, e.g., photophysical[7] and electrochemical[8] properties.[9,10] In the ground state, most fullerene derivatives possess strong absorptions in the UV region and weaker but significant absorptions over most of the visible region, where the singlet and the triplet excited states also absorb.[7,11] In addition, C_{60} and its derivatives are excellent three-dimensional electron acceptors and possess a low reorganization energy.[11−13] These characteristics offer the advantage of preparing fullerene-based dyads or triads in which photoinduced charge transfer is accelerated and charge recombination is decelerated.[7,10,12,14,15] Additionally, heterogeneous mixtures of C_{60} with a number of conjugated polymers have led to the production of plastic solar cells, which have just started to be developed.[16−19] C_{60} is also a promising nonlinear optical material, as shown in optical-limiting experiments, with performances comparable to those of other classes of useful materials.[20]

On the other hand, there have been many suggestions for the use of these molecules in medicinal chemistry.[5,6,21] The introduction of polar groups onto the sphere of C_{60} gives rise to an increased solubility of the fullerene derivatives in polar solvents, a condition necessary for performing biological tests.

In most cases, a specific functionalization type of C_{60} is required, using purpose-tailored approaches. In this paper, we demonstrate how a common intermediate can be conveniently used to reach different objectives. In particular, we focus on the synthesis of the amino-functionalized synthons (**A**) (Chart 1) and their conversion into the useful derivatives (**B**−**E**), containing the correct functionalities for the desired applications. The presence of a silicon alkoxide group on C_{60} (**B**) guarantees the homogeneous grafting of the resulting fullerene derivatives to glassy matrixes using sol−gel processing. In fact, we have recently shown that the nonlinear optical properties of C_{60} are retained after incorporation in thin glassy films.[22,23] To increase the optical-limiting performance while avoiding the formation of clusters, the functionalization of C_{60} with silicon alkoxide end groups was necessary.

A methodology for the preparation of well-ordered photoactive thin films is the self-assembly of suitably functionalized derivatives. By this method, the corresponding molecules of interest chemically bind onto

† In memory of our former lab mate, Sonia Merlo (1972-2000), whose young and exuberant life was interrupted so early and abruptly.

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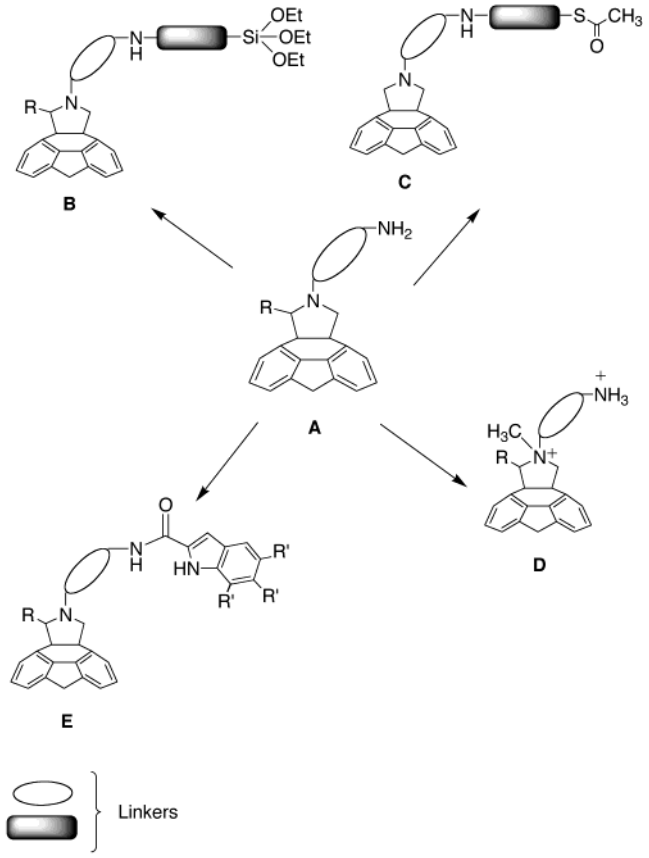
Chart 1

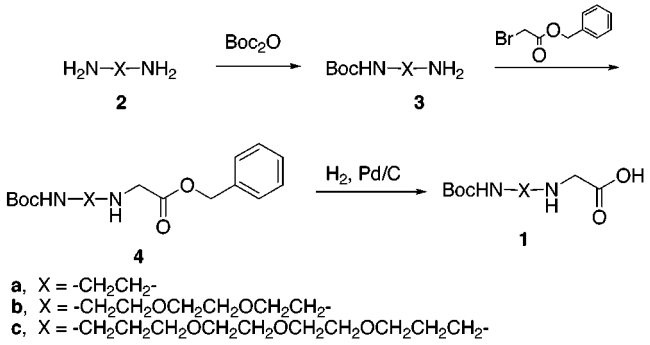


surfaces forming highly organized monolayers. The formation of self-assembled monolayers (SAM) of C_{60}-based dyads and triads containing a thiol group onto gold electrodes has been successfully reported, producing photoactive elements with high quantum yields.[24−26] The fabrication of solid-contact ion-selective electrodes using SAM of a redox-active C_{60}-attached alkanethiol compound was also recently reported.[27] In this context, a thiol-functionalized fullerene derivative (**C**) can be prepared through the condensation of **A** with the appropriate carboxylic acid containing a thiol-protected group.

A major problem for the development of fullerenes in biology is represented by the insolubility of C_{60} in biological fluids. For this reason, one of the aims of the chemical modification of fullerene is the introduction of polar chains.[28,29] Positively charged fullerene derivatives (**D**) give enhanced polarity and high affinity for biological membranes.[30] They are relatively easily prepared through the methylation of **A**.

A particularly interesting biological application of fullerene derivatives is related to the DNA photocleavage

Scheme 1



a, X = -CH_2CH_2-
b, X = -$CH_2CH_2OCH_2CH_2OCH_2CH_2$-
c, X = -$CH_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2CH_2$-

ability of C_{60} derivatives.[31,32] In principle, the action can be rendered more specific if conjugation with DNA minor-groove binders, such as trimethoxyindole,[33] is achieved.[34] In fact, it is well-known that this unit, in a manner characteristic of a class of natural antibiotics named duocarmycins, confers high affinity and selectivity for the minor groove in AT-rich sequences of DNA.[35] Condensation of the common intermediate (**A**) with heterocyclic carboxylic acids leads to the novel DNA probes (**E**).

Results and Discussion

The general synthetic strategy should allow the easy preparation of a common intermediate, characterized by the presence of a reactive group, which should permit functionalization by general methods. Given the many easy ways to perform an amide linkage under standard peptide chemistry, we focused on the synthesis of an amino-functionalized fullerene as an intermediate. This can be achieved by means of 1,3-dipolar cycloaddition of azomethine ylides to C_{60}[36,37] using different commercially available or readily synthesized aldehydes and N-(*ω*-amino)-functionalized amino acids prepared through the alkylation of monoprotected diamines. For this purpose and for obtaining spacers of different lengths, we have synthesized the α-amino acids **1a**−**c** in three synthetic steps (Scheme 1). The Boc-monoprotected diamines **3a**−**c**, prepared by starting from diamines **2a**−**c** and di-*tert*-butyl dicarbonate in dioxane, were allowed to react with benzyl bromoacetate and triethylamine in dioxane at 0 °C to give the corresponding glycine benzyl esters **4a**−**c**. Hydrogenolysis of **4a**−**c** in the presence of catalytic Pd/C in methanol afforded the corresponding α-amino acids **1a**−**c**.

Thus, α-amino acids **1a**−**c** were allowed to react with formaldehyde **5**, ferrocene carboxaldehyde (Fc-CHO) **6**, and triethylene glycol aldehyde **7** ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CHO$ = mTEG-CHO)[38] and C_{60} in refluxing toluene to form a variety of N-Boc-protected amino

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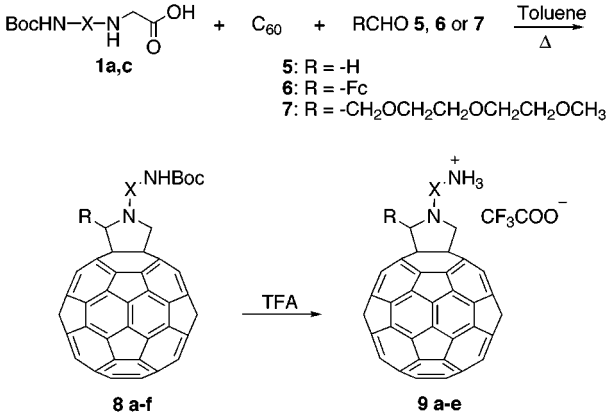
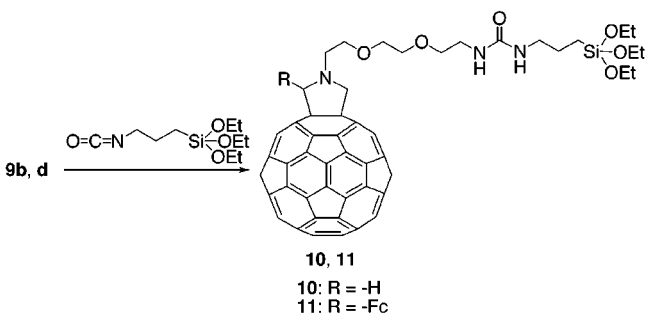
Scheme 2



a, X = $-CH_2CH_2-$, R = -H
b, X = $-CH_2CH_2OCH_2CH_2OCH_2CH_2-$, R = -H
c, X = $-CH_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2CH_2-$, R = -H
d, X = $-CH_2CH_2OCH_2CH_2OCH_2CH_2-$, R = -Fc
e, X = $-CH_2CH_2-$, R = $-CH_2OCH_2CH_2OCH_2CH_2OCH_3$
f, X = $-CH_2CH_2OCH_2CH_2OCH_2CH_2-$, R = $-CH_2OCH_2CH_2OCH_2CH_2OCH_3$

Scheme 3



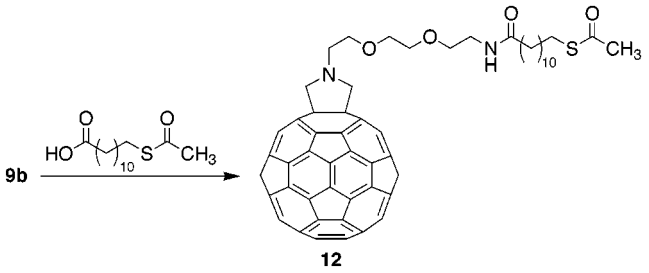
fulleropyrrolidines **8a**−**f** in good yields. Removal of the *N-tert*-butoxycarbonyl protecting group, using trifluoroacetic acid in CH_2Cl_2, gave the corresponding ammonium-fulleropyrrolidine salts **9a**−**e** that can react readily with many different compounds.

For example, we have first utilized the newly synthesized intermediates **9b** and **9d** to introduce a silicon alkoxide functionality onto C_{60} in a simple reaction step. Ammonium-fulleropyrrolidine salts **9b** and **9d** reacted readily with 3-(triethoxysilyl)propyl isocyanate in CH_2Cl_2 in the presence of triethylamine to afford the desired triethoxysilyl fulleropyrrolidines **10** and **11** in high yields (Scheme 3). These substrates are ideally suited for incorporation in sol−gel glasses for optical-limiting purposes.[23]

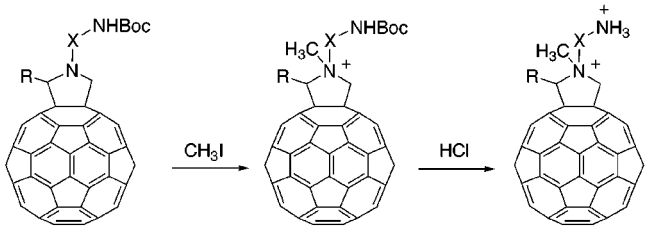
Using compound **9b**, we could easily introduce a chain onto C_{60} containing a protected thiol group for SAM purposes through condensation with 12-acetylsulfanildodecanoic acid in the presence of EDC and HOBt (Scheme 4), thus affording fulleropyrrolidine **12** in a high yield. An efficient entry into the deprotection of thiol esters in fullerene derivatives has been recently described[27] and shows that, in principle, compound **12** may be conveniently used as a thiol precursor for thin-films preparation.

Positively charged fullerene derivatives have shown excellent growth inhibition properties against a number of microorganisms, in particular, resistant strains of

Scheme 4

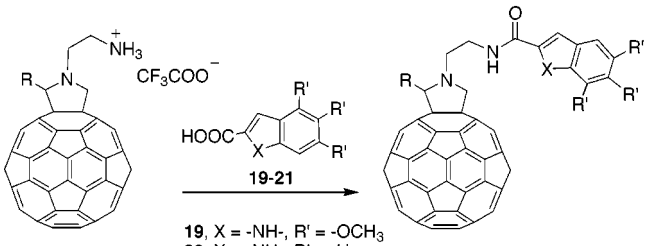


Scheme 5



13, **16**, X = $-CH_2CH_2OCH_2CH_2OCH_2CH_2-$, R = -H
14, **17**, X = $-CH_2CH_2OCH_2CH_2OCH_2CH_2-$, R = $-CH_2OCH_2CH_2OCH_2CH_2OCH_3$
15, **18**, X = $-CH_2CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2CH_2-$, R = -H

Scheme 6



19, X = -NH-, R' = $-OCH_3$
20, X = -NH-, R' = -H
21, X = -O-, R' = -H

22: R = -H, X = -NH-, R' = $-OCH_3$
23: R = $-CH_2OCH_2CH_2OCH_2CH_2OCH_3$, X = -NH-, R' = $-OCH_3$
24: R = $-CH_2OCH_2CH_2OCH_2CH_2OCH_3$, X = -NH-, R' = -H
25: R = -H, X = -O-, R' = -H

Mycobacteria.[30] Compounds **8b**, **8c**, and **8f** were easily methylated using methyl iodide in chloroform at 80 °C, and the resulting salts were deprotected using HCl gas in a methanol solution, affording derivatives **16**−**18** (Scheme 5).

The presence of two positive charges, along with the increasing number of oxygen atoms, enhanced the solubility in polar solvents, including water.

Compounds **9a** and **9e** could be condensed with the appropriate carboxylic acid **19**−**21** using EDC and HOBt as condensing agents to afford the desired compounds **22**−**25** in good yields (Scheme 6).

These derivatives can be considered bifunctional photoprobes (C_{60} and DNA minor-groove binder). Further developments of this strategy will include water solubilization through conjugation with oligonucleotides or other biologically relevant moieties.[34]

Conclusions

We have described the synthesis of three amino acids that readily add to C_{60} in the presence of various aldehydes, leading to amino-functionalized derivatives. To show the versatility and potential uses of these novel

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intermediates, we have prepared a number of compounds for studies in materials science and medicinal chemistry.

Experimental Section

General. FT-IR spectra were recorded using NaCl cells (oils) or KBr powder (DRIFT system). ^{1}H and ^{13}C spectra were recorded at 200 and 50 MHz, respectively, in $CDCl_3$ unless otherwise noted. Chemical shifts are given in parts per million (δ) relative to that of tetramethylsilane. To record ES-MS spectra, the compounds were dissolved in 4/1 THF/methanol unless otherwise noted. Yields in the azomethine ylide cycloadditions are reported as absolute values without taking into account C_{60} recovery (30−40% of the initial fullerene was routinely recovered). C_{60} was purchased from Bucky-USA (99.5%), and all other reagents and solvents were used as purchased from Fluka, Aldrich, J. T. Baker, and Cambridge Isotope Laboratories. The silica gel NM Kieselgel 60 (70−230 mesh ASTM) was obtained from Macherey-Nagel and was used as the support for any column chromatographies. Monoprotected diammines **3a**−**c**,[39−41] 12-acetylsulfanildodecanoic acid,[42] 4,5,6-trimethoxy-indole-2-carboxylic acid **20**,[33] and benzofuran-2-carboxylic acid **21**[43] were prepared according to the literature. All the fullerene derivatives are brown solids.

Synthesis of 4a−c: General Procedure. To a solution of **3a**−**c** (0.03 mol) in 1,4-dioxane (20 mL) at 0 °C was added a solution of benzyl bromoacetate (2.3 g, 0.01 mol) in 1,4-dioxane (30 mL) over a period of 1 h, and the reaction mixture was stirred overnight. The solvent was evaporated under reduced pressure, and the residue was dissolved in water (70 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic phase was dried over Na_2SO_4, and the solvent was removed under vacuum. The crude residue was purified by chromatography (1/1 EtOAc/petroleum ether followed by pure EtOAc) to afford the desired compounds **4** as colorless oils.

4a. $C_{16}H_{24}N_2O_4$ (MW 308.38), yield: 70% (2.2 g, 7.02 mmol). FT-IR: cm^{-1} 3347, 2974, 2930, 1738, 1694, 1517, 1170, 968, 751. ^{1}H NMR: δ 7.36 (s, 5H), 5.17 (s, 2H), 4.98 (bs, 1H), 3.45 (s, 2H), 3.19 (m, 2H), 2.74 (t, J = 5.9 Hz, 2H), 1.44 (s, 9H). ^{13}C NMR: δ 172.3, 156.0, 135.4, 128.5, 128.3, 128.3, 79.1, 68.0, 66.6, 50.4, 49.7, 28.3. EI-MS: m/z 308 (M^+, 30%), 253 (8%), 91 (100%).

4b. $C_{20}H_{32}N_2O_6$ (MW 396.49), yield: 84% (3.3 g, 8.40 mmol). FT-IR: cm^{-1} 3347, 2871, 1712, 1512, 1458, 1368, 1248, 1175, 966, 865, 747, 701. ^{1}H NMR: δ 7.32 (m, 5H), 5.21 (bs, 1H), 5.15 (s, 2H), 3.59−3.51 (m, 6H), 3.51−3.46 (m, 4H), 3.28 (m, 2H), 2.78 (t, J = 5.2 Hz, 2H), 1.41 (s, 9H). ^{13}C NMR: δ 172.1, 155.9, 135.5, 128.5, 128.2, 79.0, 70.6, 70.2, 70.1, 66.5, 50.8, 48.6, 40.4, 40.3, 28.5. EI-MS: m/z 396 (M^+, 20%), 205 (100%), 161 (40%), 91 (55%).

4c. $C_{24}H_{40}N_2O_7$ (MW 468.59), yield: 69% (3.2 g, 6.89 mmol). FT-IR: cm^{-1} 3342, 2928, 2868, 1707, 1518, 1458, 1359, 1252, 1174, 976, 866, 746, 702. ^{1}H NMR: δ 7.33 (s, 5H), 5.13 (s, 2H), 5.06 (bs, 1H), 3.61−3.47 (m, 12H), 3.41 (s, 2H), 3.18 (q, J = 6.2 Hz, 2H), 2.66 (t, J = 6.7 Hz, 2H), 1.84−1.66 (m, 4H), 1.41 (s, 9H). ^{13}C NMR: δ 172.4, 156.1, 135.6, 128.6, 128.4, 127.0, 79.0, 70.7, 70.3, 69.7, 65.6, 51.1, 47.0, 38.6, 30.1, 29.7, 28.6. EI-MS: m/z 468 (M^+, 10%), 395 (10%), 367 (5%), 277 (60%), 233 (30%), 178 (100%), 92 (40%), 73 (30%), 59 (40%).

Synthesis of Compounds 1a−c: General Procedure. To a methanol solution (50 mL) of **4** (5.05 mmol) was added 50.0 mg of 10% Pd/C, and the mixture was stirred under a hydrogen atmosphere for 24 h. The catalyst was removed by filtration on Celite, and the solvent was evaporated. The pure product was triturated in diethyl ether to give a white solid.

1a. Data were in agreement with the literature.[39]

1b. $C_{13}H_{26}N_2O_6$ (MW 306.36), yield: 99% (1.6 g, 5.05 mmol). Mp: 105−106 °C. IR-DRIFT: cm^{-1} 3250, 2970, 1706, 1620, 1540, 1365, 1115, 686, 590, 480. ^{1}H NMR: δ 8.21 (bs, 1H), 6.23 (bs, 1H), 5.54 (bt, 1H), 3.79 (bt, 2H), 3.64−3.53 (m, 8H), 3.49 (t, J = 5.1 Hz, 2H), 3.22 (m, 2H), 1.40 (s, 9H). ^{13}C NMR: δ 170.5, 156.2, 79.1, 70.4, 70.3, 70.1, 66.6, 49.8, 46.8, 40.4, 28.6. EI-MS: m/z 306 (M^+). Anal. Calcd for $C_{13}H_{26}N_2O_6$: C, 50.97; H, 8.55; N, 9.14. Found: C, 51.10; H, 8.65; N, 9.16.

1c. $C_{17}H_{34}N_2O_7$ (MW 378.49), yield: 99% (1.9 g, 5.05 mmol). Mp: 121−123 °C. IR-DRIFT: cm^{-1} 3338, 3079, 2875, 2230, 1674, 1562, 1382, 1279, 1107, 857. ^{1}H NMR: δ 5.27 (bs, 1H), 3.73−3.33 (m, 14H), 3.28−2.99 (m, 4H), 2.00 (m, J = 5.8 Hz, 2H), 1.71 (m, J = 6.4 Hz, 2H), 1.39 (s, 9H). ^{13}C NMR: δ 170.1, 156.1, 78.9, 70.6, 70.5, 70.4, 70.2, 69.5, 69.0, 50.0, 46.1, 38.6, 29.8, 28.6, 26.3. ES-MS (MeOH): m/z 379 (MH^+).

Synthesis of Compounds 8a−f: General Procedure. A toluene solution (300 mL) of C_{60} (500.0 mg, 0.69 mmol) and the appropriate aldehyde (3.45 mmol) and amino acid **1a**−**c** (1.38 mmol) was heated to reflux for 1 h. After cooling to room temperature, the product was purified by column chromatography. The brown solids were dissolved in CH_2Cl_2 and precipitated by addition of MeOH.

8a. $C_{69}H_{18}N_2O_2$ (MW 906.93), yield: 42% (264.7 mg, 0.29 mmol). Eluant: 95/5 toluene/AcOEt. IR-DRIFT: cm^{-1} 3355, 2980, 2790, 1705, 1510, 1120, 770, 525, 475. ^{1}H NMR: δ 5.25 (bs, 1H), 4.45 (s, 4H), 3.67 (m, 2H), 3.24 (t, J = 5.9 Hz, 2H), 1.49 (s, 9H). ^{13}C NMR: δ 154.8, 149.1, 147.3, 146.3, 146.1, 146.0, 145.7, 145.5, 145.3, 144.6, 143.1, 142.7, 142.2, 142.1, 141.9, 140.2, 136.3, 70.7, 67.9, 66.0, 54.4, 28.6. UV−vis (cyclohexane): λ_{max} nm 427, 327, 272. ES-MS: m/z 907 (MH^+). Anal. Calcd for $C_{69}H_{18}N_2O_2$: C, 91.38; H, 2.00; N, 3.09. Found: C, 84.70; H, 2.24; N, 2.74.

8b. $C_{73}H_{26}N_2O_4$ (MW 995.03), yield: 31% (212.2 mg, 0.21 mmol). Eluant: 9/1 toluene/AcOEt. IR-DRIFT: cm^{-1} 3444, 2921, 2853, 1710, 1498, 1457, 1168, 1121, 794, 545. ^{1}H NMR: δ 5.08 (bs, 1H), 4.50 (s, 4H), 4.05 (t, J = 5.5 Hz, 2H), 3.77 (m, 4H), 3.60 (t, J = 5.3 Hz, 2H), 3.36 (m, 4H), 1.44 (s, 9H). ^{13}C NMR: δ 156.0, 155.1, 147.3, 146.3, 146.1, 145.7, 145.4, 145.3, 144.6, 143.1, 142.7, 142.3, 142.1, 141.9, 140.2, 136.2, 79.3, 70.9, 70.7, 70.6, 70.5, 68.6, 54.4, 28.6. UV−vis (cyclohexane): λ_{max} nm 703, 546 (sh), 466 (sh), 429, 309, 254. ES-MS: m/z 995 (MH^+). Anal. Calcd for $C_{73}H_{26}N_2O_4$: C, 88.12; H, 2.63; N, 2.82. Found: C, 88.20; H, 2.59; N, 2.82.

8c. $C_{77}H_{34}N_2O_5$ (MW 1067.14), yield: 20% (147.3 mg, 0.14 mmol). Eluant: 95/5 toluene/iPrOH. IR-DRIFT: cm^{-1} 3327, 2975, 2874, 2783, 1707, 1505, 1249, 1114, 880, 767. ^{1}H NMR: δ 5.00 (bs, 1H), 4.40 (s, 4H), 3.82 (t, J = 6.5 Hz, 2H), 3.73−3.51 (m, 10H), 3.27−3.14 (m, 4H), 2.21 (m, J = 6.5 Hz, 2H), 1.76 (m, J = 6.3 Hz, 2H) 1.42 (s, 9H). ^{13}C NMR: δ 156.1, 155.0, 147.3, 146.3, 146.1, 145.7, 145.4, 145.3, 144.6, 143.1, 142.7, 142.3, 142.1, 141.9, 140.2, 136.3, 79.0, 70.8, 70.7, 70.5, 70.4, 69.8, 69.6, 68.0, 51.9, 38.8, 29.8, 29.1, 28.6. UV−vis (THF): λ_{max} nm 705, 431, 327, 255. ES-MS: m/z 1067 (MH^+), 1090 ($M + Na)^+$. Anal. Calcd for $C_{77}H_{34}N_2O_5$: C, 86.67; H, 3.21; N, 2.63. Found: C, 82.40; H, 3.24; N, 2.59.

8d. $C_{83}H_{34}FeN_2O_4$ (MW 1179.05), yield: 31% (252.0 mg, 0.21 mmol). Eluant: 96/4 toluene/AcOEt. IR-DRIFT: cm^{-1} 3440, 3370, 2920, 2862, 1709, 1512, 1250, 1169, 1115, 821, 494. ^{1}H NMR: δ 5.10 (d, J = 10.0 Hz, 1H), 5.02 (s, 1H), 5.00 (bt, 1H), 4.56 (s, 1H), 4.50 (s, 1H), 4.30 (s, 5H), 4.21 (m, 5H), 3.93 (m, 2H), 3.78 (m, 2H), 3.63 (m, 2H), 3.34 (m, 2H), 3.16 (m, 2H), 1.44 (s, 9H). ^{13}C NMR: δ 156.4, 156.0, 154.4, 153.9, 153.4, 147.6, 147.2, 146.5, 146.2, 146.1, 146.1, 145.9, 145.8, 145.6, 145.5, 145.3, 145.2, 144.7, 144.7, 144.4, 143.1, 143.0, 142.7, 142.6, 142.2, 142.1, 141.9, 141.8, 141.6, 141.4, 140.2, 140.1, 139.4, 138.8, 136.5, 136.3, 135.9, 135.7, 87.0, 79.4, 71.1, 71.0, 70.6, 69.5, 68.8, 68.5, 68.3, 67.6, 67.6, 67.3, 53.4, 28.6. UV−vis (toluene): λ_{max} nm 704, 432, 329, 309. ES-MS: m/z 1179 (MH^+). Anal. Calcd for $C_{83}H_{34}FeN_2O_4$: C, 84.55; H, 2.91; N, 2.38. Found: C, 84.20; H, 3.03; N, 2.37.

8e. $C_{75}H_{30}N_2O_5$ (MW 1039.09), yield: 17% (121.9 mg, 0.12 mmol). Eluant: 99/1 toluene/iPrOH. IR-DRIFT: cm^{-1} 3365,

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2918, 1710, 1517, 1171, 856, 770, 574, 527. ^{1}H NMR: δ 5.52 (bs, 1H), 4.88 (d, J = 9.7 Hz, 1H), 4.58 (dd, J = 9.8 and 3.3 Hz, 1H), 4.44 (m, 1H), 4.38−4.18 (m, 2H), 3.86−3.40 (m, 10H), 3.38 (s, 3H), 3.12 (m, 2H), 1.53 (s, 9H). ^{13}C NMR: δ 156.9, 153.9, 149.5, 148.7, 147.8, 147.3, 147.2, 146.8, 146.4, 146.3, 146.3, 146.2, 146.2, 146.1, 146.0, 145.8, 145.6, 145.5, 145.4, 145.3, 145.2, 145.2, 144.8, 144.6, 144.4, 143.2, 143.1, 142.7, 142.7, 142.2, 142.0, 141.7, 140.6, 140.3, 140.2, 139.8, 139.5, 135.6, 79.4, 74.5, 74.1, 73.7, 72.5, 72.1, 71.0, 70.7, 70.1, 66.8, 59.2, 28.7. UV−vis (cyclohexane): λ_{max} nm 701, 430, 328, 270, 261. ES-MS: m/z 1039 (MH^+). Anal. Calcd for $C_{75}H_{30}N_2O_5$: C, 86.69; H, 2.91; N, 2.70. Found: C, 85.00; H, 3.06; N, 2.65.

8f. $C_{79}H_{38}N_2O_7$ (MW 1127.19), yield: 44% (213.2 mg, 0.19 mol). Eluant: 98/2 toluene/iPrOH. IR-DRIFT: cm^{-1} 3350, 2878, 1710, 1115, 488. ^{1}H NMR: δ 5.03 (bs, 1H), 4.95 (d, J = 4.8 Hz, 1H), 4.55 (m, 1H), 4.37 (m, 2H), 4.25 (d, J = 4.8 Hz, 1H), 4.03 (t, J = 5.5 Hz, 2H), 3.83−3.68 (m, 8H), 3.64−3.52 (m, 4H), 3.52−3.45 (m, 4H), 3.34 (s, 3H), 3.16 (m, 2H), 1.42 (s, 9H). ^{13}C NMR: δ 155.9, 155.8, 154.6, 153.9, 152.4, 147.1, 147.1, 147.0, 146.2, 146.1, 146.0, 145.9, 145.7, 145.6, 145.5, 145.4, 145.3, 145.2, 145.1, 144.6, 144.5, 144.3, 143.1, 142.9, 142.5, 142.1, 142.0, 141.9, 141.6, 141.5, 140.2, 140.1, 139.6, 139.2, 137.2, 136.3, 135.8, 135.4, 79.2, 74.7, 73.4, 72.1, 71.9, 70.8, 70.5, 70.4, 70.4, 70.2, 70.0, 67.7, 59.2, 59.0, 52.2, 40.4, 28.5. UV−vis (CH_2Cl_2): λ_{max} nm 702, 638 (sh), 470 (sh), 430, 329, 307. ES-MS: m/z 1127 (MH^+), 1165 ($M + K)^+$. Anal. Calcd for $C_{79}H_{38}N_2O_7$: C, 84.18; H, 3.40; N, 2.49. Found: C, 84.00; H, 3.53; N, 2.50.

Synthesis of Compounds 9a−e: General Procedure. A solution of **8** (0.15 mmol) in CH_2Cl_2 (3 mL) and CF_3COOH (3 mL) was stirred at room temperature for 3 h. The solvent and the acid in excess were removed in vacuo. The solid residue was washed with toluene in order to remove any trace of starting material and then dried under vacuum.

9a. $C_{68}H_{12}F_6N_2O_4$ (MW 1034.86), yield: 99% (155.2 mg, 0.15 mmol). UV−vis (THF): λ_{max} nm 704, 431, 326, 255. ES-MS: m/z 806 (M^+). Anal. Calcd for $C_{68}H_{12}F_6N_2O_4$: C, 78.92; H, 1.17; N, 2.71. Found: C, 76.10; H, 1.17; N, 2.54.

9b. $C_{72}H_{20}F_6N_2O_6$ (MW 1122.96), yield: 99% (167.8 mg, 0.15 mmol). IR-DRIFT: cm^{-1} 2890, 1680, 1515, 1480, 1190, 1130, 715, 525. ^{1}H NMR (DMSO-d_6): δ 7.81 (bs, 3H), 4.58 (s, 4H), 3.93 (t, J = 5.5 Hz, 2H), 3.71−3.43 (m, 6H), 3.32 (m, 2H), 2.95 (m, 2H). ^{13}C NMR (DMSO-d_6): δ 156.0, 147.4, 146.7, 146.4, 146.2, 146.0, 145.5, 145.4, 144.7, 143.3, 142.8, 142.5, 142.2, 142.0, 140.2, 136.4, 135.4, 71.5, 70.5, 70.1, 68.0, 67.5, 54.1. UV−vis (cyclohexane): λ_{max} nm 684, 484 (sh), 430, 331. ES-MS: m/z 896 (M^+). Anal. Calcd for $C_{72}H_{20}F_6N_2O_6$: C, 77.01; H, 1.80; N, 2.49. Found: C, 77.30; H, 1.56; N, 2.58.

9c. $C_{76}H_{28}F_6N_2O_7$ (MW 1195.07), yield: 99% (178.1 mg, 0.15 mmol). IR-DRIFT: cm^{-1} 3732, 2996, 2879, 2771, 1682, 1477, 1429, 1200, 1125, 836, 721, 632. ^{1}H NMR (DMSO-d_6): δ 7.16 (bs, 3H), 4.43 (s, 4H), 3.70 (t, J = 6.6 Hz, 2H), 3.61−3.32 (m, 10H), 3.11 (t, J = 6.6 Hz, 2H), 2.83 (m, 2H), 2.08 (m, J = 6.6 Hz, 2H), 1.75 (m, J = 6.8 Hz, 2H). ^{13}C NMR (DMSO-d_6): δ 156.2, 147.4, 146.8, 146.4, 146.2, 146.0, 145.5, 145.4, 144.8, 143.3, 142.8, 142.5, 142.2, 142.0, 140.2, 136.4, 71.5, 70.6, 70.5, 70.3, 69.3, 68.1, 67.8, 51.6, 37.6, 29.3, 27.9. UV−vis (THF): λ_{max} nm 705, 431, 328, 255. ES-MS: m/z 968 (M^+), 484 (M^{2+}). Anal. Calcd for $C_{76}H_{28}F_6N_2O_7$: C, 76.38; H, 2.36; N, 2.34. Found: C, 74.70; H, 2.38; N, 2.44.

9d. $C_{80}H_{27}F_3FeN_2O_4$ (MW 1192.96), yield: 90% (161.0 mg, 0.14 mmol). IR-DRIFT: cm^{-1} 3519, 3440, 2775, 1679, 1435, 1188, 1134, 825, 719. ^{1}H NMR: δ 7.80 (m, 3H), 5.15 (d, J = 9.5 Hz, 1H), 5.12 (s, 1H), 4.91 (m, 1H), 4.50 (s, 2H), 4.33 (s, 5H), 4.28 (s, 2H), 4.23 (d, J = 9.5 Hz, 1H), 4.11 (bt, 2H), 3.84 (m, 2H), 3.71 (m, 4H), 3.15 (m, 1H), 2.96 (m, 2H). ^{13}C NMR (DMSO-d_6): δ 154.2, 149.7, 147.8, 147.4, 147.1, 146.4, 146.1, 145.6, 145.4, 144.9, 143.2, 142.7, 142.4, 140.2, 136.5, 136.3, 129.6, 128.9, 87.4, 78.1, 70.6, 70.1, 69.4, 68.0, 67.6. UV−vis (THF): λ_{max} nm 703, 430, 325, 304, 255. ES-MS: m/z 1080 (M^+). Anal. Calcd for $C_{80}H_{27}F_3FeN_2O_4$: C, 80.55; H, 2.28; N, 2.35. Found: C, 78.00; H, 2.24; N, 2.30.

9e. $C_{72}H_{23}F_3N_2O_5$ (MW 1052.99), yield: 99% (156.9 mg, 0.15 mmol). UV−vis (THF): λ_{max} nm 700, 463 (sh), 430, 327, 272, 255. ES-MS: m/z 939 (M^+). Anal. Calcd for $C_{72}H_{23}F_3N_2O_5$: C, 82.13; H, 2.20; N, 2.66. Found: C, 80.95; H, 2.19; N, 2.58.

Synthesis of Compounds 10 and 11: General Procedure. To a mixture of **9b** or **9d** (14.9 mmol) in 30 mL of CH_2Cl_2 was added 41 μL (29.8 mmol) of TEA. After the mixture was stirred for 10 min at room temperature, 37.0 mg (14.9 mmol) of 3-(triethoxysilyl)propyl isocyanate was introduced and the whole mixture was left to stir for 16 h at room temperature. After filtration, the solvent was evaporated, and the solid was washed and centrifuged four times with diethyl ether and eventually dried.

10. $C_{78}H_{39}N_3O_6Si$ (MW 1142.25), yield: 89% (151.5 mg, 0.13 mmol). IR-DRIFT: cm^{-1} 3359, 2882, 1631, 1567, 1427, 1081, 954, 768. ^{1}H NMR (400 MHz): δ 4.84 (bt, 1H), 4.70 (bt, 1H), 4.51 (s, 4H), 4.05 (t, J = 5.0 Hz, 2H), 3.85−3.72 (m, 10H), 3.61 (t, J = 5.0 Hz, 2H), 3.41−3.34 (m, 4H), 3.16 (q, J = 7.0 Hz, 2H), 1.66−1.56 (m, 2H), 1.21 (t, J = 7.0 Hz, 9H), 0.63 (t, J = 8.4 Hz, 2H). ^{13}C NMR: δ 158.4, 154.9, 147.3, 146.3, 146.1, 146.0, 145.7, 145.4, 145.3, 144.6, 143.2, 142.7, 142.2, 142.1, 141.9, 140.2, 136.2, 70.9, 70.4, 68.7, 58.8, 58.6, 43.2, 23.8, 18.5, 7.9. UV−vis (toluene): λ_{max} nm 703, 432, 326. ES-MS: m/z 1142 (MH^+). Anal. Calcd for $C_{78}H_{39}N_3O_6Si$: C, 82.02; H, 3.44; N, 3.68. Found: C, 80.40; H, 3.39; N, 3.60.

11. $C_{88}H_{47}FeN_3O_6Si$ (MW 1326.30), yield: 93% (153.2 mg, 0.11 mmol). IR-DRIFT: cm^{-1} 3384, 2972, 2915, 1671, 1560, 1458, 1173, 1116, 902, 800, 769. ^{1}H NMR (400 MHz): δ 5.09 (d, J = 9.2 Hz, 1H), 5.03 (s, 1H), 4.67 (bt, 1H), 4.57 (s, 1H), 4.50 (s, 1H), 4.39 (bt, 1H), 4.32 (s, 5H), 4.26 (s, 1H), 4.20 (m, 4H), 3.92 (m, 2H), 3.80 (m, 8H), 3.63 (t, J = 5.1 Hz, 2H), 3.39 (m, 2H), 3.17 (m, 2H), 3.10 (q, J = 6.2 Hz, 2H), 1.56 (m, 2H), 1.21 (t, J = 6.9 Hz, 9H), 0.60 (t, J = 8.4 Hz, 2H). ^{13}C NMR: δ 158.1, 156.3, 154.3, 153.8, 153.3, 147.5, 147.3, 146.5, 146.3, 145.9, 145.8, 145.6, 145.4, 145.2, 145.2, 144.7, 144.4, 143.0, 142.7, 142.6, 142.2, 142.1, 141.8, 141.6, 141.4, 140.2, 139.4, 138.8, 136.5, 135.9, 135.7, 97.2, 87.1, 70.9, 79.6, 78.8, 78.4, 77.7, 67.3, 58.6, 23.8, 18.5. UV−vis (toluene): λ_{max} nm 432, 329. ES-MS: m/z 1326 (MH^+). Anal. Calcd for $C_{88}H_{47}FeN_3O_6Si$: C, 79.69; H, 3.57; N, 3.17. Found: C, 78.80; H, 3.53; N, 3.15.

Synthesis of Compound 12. A solution containing 12-acetylsulfanildodecanoic acid (20.9 mg, 0.08 mmol), EDC·HCl (29.3 mg, 0.15 mmol), and HOBT (16.9 mg, 0.15 mmol) was stirred in CH_2Cl_2 (5 mL) at room temperature for 30 min. To this solution was slowly added a mixture of fullerene derivative **9b** (85.3 mg, 0.076 mmol) and NEt_3 (28 μL, 0.23 mmol) in CH_2Cl_2 (5 mL). The resulting reaction mixture was stirred for 12 h at room temperature. The solvent was then evaporated under reduced pressure, and the product was purified by chromatography on silica gel using 9/1 toluene/AcOEt as the eluant.

12. $C_{82}H_{42}N_2O_4S$ (MW 1151.32), yield: 53% (46.2 mg, 0.04 mmol). FT-IR: cm^{-1} 3330, 2923, 2851, 1688, 1540, 1460, 1428, 1341, 1184, 1118, 954, 767. ^{1}H NMR: δ 6.12 (bt, 1H), 4.52 (s, 4H), 4.06 (t, J = 5.7 Hz, 2H), 3.83 (m, 2H), 3.74 (m, 2H), 3.61 (m, 2H), 3.48 (m, 2H), 3.39 (m, 2H), 2.83 (t, J = 7.3 Hz, 2H), 2.31 (s, 3H), 2.17 (dd, J = 4.4 and 8.1 Hz, 2H), 1.56 (m, 4H), 1.24 (m, 14H). ^{13}C NMR: δ 196.1, 173.2, 154.9, 147.3, 146.3, 146.1, 146.0, 145.7, 145.5, 145.3, 144.6, 143.2, 142.7, 142.2, 142.1, 141.9, 140.2, 136.2, 76.5, 70.8, 70.6, 70.4, 70.2, 68.6, 54.5, 39.3, 37.0, 30.8, 29.7, 29.6, 29.6, 29.5, 29.3, 29.3, 29.0, 25.9. UV−vis (toluene): λ_{max} nm 704, 433, 327, 309. ES-MS: m/z 1151 (MH^+). Anal. Calcd $C_{82}H_{42}N_2O_4S$: C, 85.55; H, 3.68; N, 2.43. Found: C, 85.20; H, 3.57; N, 2.45.

Synthesis of Compounds 13−15: General Procedure. Compound **8b**, **8c**, or **8f** (0.04 mmol) was dissolved in 10 mL of $CHCl_3$, and 275 μL (4.40 mmol) of CH_3I was added. The solution was stirred in closed vials for 72 h at 80 °C. The excess of methyl iodide and solvent were removed by evaporation, and the residue was dried under vacuum.

13. $C_{74}H_{29}IN_2O_4$ (MW 1136.94), yield: 99% (45.5 mg, 0.04 mmol). IR-DRIFT: cm^{-1} 3340, 2970, 1690, 1513, 1112, 767, 521. ^{1}H NMR (DMSO-d_6): δ 5.75 (m, 4H), 4.45 (m, 2H), 4.24 (m, 2H), 4.15 (s, 3H), 3.74 (m, 2H), 3.61 (m, 2H), 3.44 (m, 2H), 3.01 (m, 2H), 1.30 (s, 9H). UV−vis (CH_2Cl_2): λ_{max} nm 688, 545 (sh), 460 (sh), 428, 317. ES-MS (1/1 CH_3CN/MeOH): m/z 1009

(M^+). Anal. Calcd for $C_{74}H_{29}IN_2O_4$: C, 78.17; H, 2.57; N, 2.46. Found: C, 73.40; H, 2.44; N, 2.38.

14. $C_{80}H_{41}IN_2O_7$ (MW 1269.13), yield: 99% (50.7 mg, 0.04 mmol). IR-DRIFT: cm^{-1} 2875, 1703, 1460, 1110, 520. ^1H NMR (two diastereoisomers in a 70/30 ratio): major isomer, δ 6.56 (d, $J = 12.5$ Hz, 1H), 5.78 (d, $J = 12.2$ Hz, 1H), 5.37 (m, 1H), 5.07−4.73 (m, 4H), 4.60−4.31 (m, 2H), 4.34 (s, 3H), 4.04−3.84 (m, 4H), 3.78−3.64 (m, 6H), 3.59−3.51 (m, 4H), 3.38 (s, 3H), 3.25 (m, 2H), 1.40 (s, 9H); minor isomer, diagnostic peaks, δ 6.65 (d, $J = 6.2$ Hz, 1H), 6.11 (d, $J = 6.2$ Hz, 1H), 4.51 (s, 3H). ^{13}C NMR: δ 155.7, 151.9, 149.5, 148.9, 148.8, 147.4, 147.3, 146.4, 146.3, 146.3, 146.3, 146.1, 146.1, 145.8, 145.8, 145.7, 145.5, 145.4, 145.1, 144.7, 144.6, 144.6, 144.5, 144.5, 144.4, 144.4, 144.2, 144.1, 143.1, 143.0, 142.8, 142.8, 142.7, 142.1, 142.1, 142.0, 141.7, 141.6, 141.0, 140.8, 140.5, 140.1, 140.0, 139.9, 137.7, 136.8, 136.3, 135.8, 79.4, 72.1, 71.8, 71.1, 70.9, 70.7, 70.4, 70.4, 70.1, 68.1, 68.0, 67.8, 66.2, 65.8, 59.1, 45.6, 40.3, 28.5. UV−vis (CH_2Cl_2): λ_{max} nm 686, 605 (sh), 462 (sh), 426, 317. ES-MS (MeOH): m/z 1142 (M^+). Anal. Calcd for $C_{80}H_{41}IN_2O_7$: C, 75.71; H, 3.26; N, 2.21. Found: C, 73.60; H, 3.12; N, 2.25.

15. $C_{78}H_{37}IN_2O_5$ (MW 1209.08), yield: 96% (46.4 mg, 0.04 mmol). IR-DRIFT: cm^{-1} 3515, 2974, 2878, 1695, 1505, 1363, 1249, 1114, 861, 768, 652. ^1H NMR (DMSO-d_6): δ 5.76 (m, 4H), 4.42−4.29 (m, 2H), 4.08 (s, 3H), 3.71 (t, $J = 5.2$ Hz, 2H), 3.64−3.24 (m, 10H), 2.98−2.86 (m, 2H), 2.45−2.37 (m, 2H), 1.56 (m, $J = 6.6$ Hz, 2H), 1.33 (s, 3H). ^{13}C NMR (DMSO-d_6): δ 153.1, 152.5, 147. 6, 146.6, 146.6, 146.3, 146.3, 145.9, 145.8, 145.7, 145.6, 145.5, 144.7, 144.6, 143.4, 143.3, 143.0, 142.9, 142.3, 142.2, 142.2, 141.7, 141.7, 140.1, 140.1, 136.71, 136.5, 78.2, 72.3, 70.6, 70.5, 70.3, 69.3, 68.9, 68.0, 63.8, 49.0, 38.1, 30.5, 29.1, 24.7. UV−vis (CH_2Cl_2): λ_{max} nm 688, 427, 316, 253. ES-MS: m/z 1081 (M^+). Anal. Calcd for $C_{78}H_{37}IN_2O_5$: C, 77.49; H, 3.08; N, 2.32. Found: C, 75.80; H, 3.09; N, 2.27.

Synthesis of Compounds 16−18: General Procedure. HCl gas was bubbled for 15 min through a methanol solution (15 mL) of **13**, **14**, or **15** (0.02 mmol) after which the solvent was removed in vacuo. The remaining solids were washed with toluene and dried under vacuum.

16. $C_{69}H_{22}ClIN_2O_2$ (MW 1073.31), yield: 99% (21.4 mg, 0.02 mmol). IR-DRIFT: cm^{-1} 3344, 2969, 1633, 1434, 1110, 520. ^1H NMR (DMSO-d_6): δ 8.02 (bs, 3H), 5.25 (bs, 4H), 4.16 (m, 2H), 3.90−3.63 (m, 11H), 2.93 (m, 2H). UV−vis (H_2O): λ_{max} nm 702, 428, 338, 262, 204. ES-MS (H_2O): m/z 910 (M^+), 455 (M^{2+}). Anal. Calcd for $C_{69}H_{22}ClIN_2O_2$: C, 77.20; H, 2.07; N, 2.61. Found: C, 77.40; H, 2.40; N, 2.58.

17. $C_{75}H_{34}ClIN_2O_5$ (MW 1205.44), yield: 99% (24.1 mg, 0.02 mmol) IR-DRIFT: cm^{-1} 3348, 2875, 1450, 1115, 525. ^1H NMR (DMSO-d_6): δ 8.12 (bs, 3H), 6.35−5.65 (series of multiplets, 3H), 4.96−4.45 (series of multiplets, 4H), 4.28−3.93 (series of multiplets, 6H), 3.84−3.26 (series of multiplets, 13H), 3.20 (s, 3H), 2.92 (m, 2H). UV−vis (H_2O): λ_{max} nm 703, 330, 258, 204. ES-MS (H_2O): m/z 1042 (M^+), 521 (M^{2+}). Anal. Calcd for $C_{75}H_{34}ClIN_2O_5$: C, 74.73; H, 2.84; N, 2.32. Found: C, 72.60; H, 2.35; N, 2.07.

18. $C_{73}H_{30}ClIN_2O_3$ (MW 1145.42), yield: 99% (22.9 mg, 0.02 mmol). IR-DRIFT: cm^{-1} 3515, 2988, 2882, 2756, 2035, 1713, 1486, 1109, 947, 768. ^1H NMR (DMSO-d_6): δ 7.99 (bs, 3H), 5.08 (m, 4H), 4.47−4.33 (m, 2H), 4.10 (s, 3H), 3.71 (t, $J = 5.2$ Hz, 2H), 3.65−3.24 (m, 10H), 2.86−2.71 (m, 2H), 2.45−2.36 (m, 2H), 1.77 (m, $J = 6.6$ Hz, 2H). ^{13}C NMR (DMSO-d_6): δ 153.2, 152.5, 147.5, 146.6, 146.5, 146.3, 146.3, 145.9, 145.9, 145.8, 145.8, 145.7, 145.6, 145.5, 144.7, 144.6, 143.4, 143.4, 143.0, 142.9, 142.7, 142.2, 142.2, 141.7, 141.7, 140.1, 140.0, 136.8, 136.6, 72.2, 70.6, 70.4, 70.2, 69.3, 68.1, 63.4, 48.9, 37.3, 27.9, 24.8. UV−vis (CH_2Cl_2): λ_{max} nm 689, 428, 317, 255. ES-MS: m/z 982 (M^+), 491 (M^{2+}). Anal. Calcd for $C_{73}H_{30}ClIN_2O_5$: C, 76.55; H, 2.64; N, 2.45. Found: C, 73.20; H, 2.73; N, 2.52.

Synthesis of Compounds 22−25: General Procedure. A solution of HOBT (20.7 mg, 0.15 mmol), EDC·HCl (29.3 mg, 0.15 mmol), and acid **19**, **20**, or **21** (0.11 mmol) in CH_2Cl_2 (10 mL) was stirred for 15 min and then added dropwise to a suspension of ammonium salt **9a** or **9e** (0.08 mmol) in CH_2Cl_2 (30 mL) and 4-methyl morpholine (17 μL, 0.15 mmol) at 0 °C. After 20 min, the mixture was washed with water and separated, and the combined organic fractions were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography. The brown solid compounds were dissolved in CH_2Cl_2 and precipitated by addition of methanol.

22. $C_{76}H_{21}N_3O_4$ (MW 1040.03), yield: 51% (40.3 mg, 0.04 mmol). Eluant: 9/1 toluene/AcOEt. IR-DRIFT: cm^{-1} 3325, 2824, 1646, 1119, 527. ^1H NMR (3/1 $CDCl_3/CS_2$): δ 9.30 (bs, 1H), 7.12 (bs, 1H), 6.84 (s, 1H), 6.66 (s, 1H), 4.53 (s, 4H), 4.04 (s, 3H), 4.01 (m, 2H), 3.85 (s, 3H), 3.81 (s, 3H), 3.44 (t, $J = 6.1$ Hz, 2H). ^{13}C NMR (3/1 $CDCl_3/CS_2$): δ 161.4, 154.4, 150.1, 147.3, 146.3, 146.1, 145.9, 145.5, 145.3, 144.6, 143.2, 142.7, 142.2, 142.1, 141.9, 140.3, 136.1, 130.6, 125.9, 123.4, 70.6, 67.4, 61.3, 61.0, 56.2, 53.0. UV−vis (cyclohexane): λ_{max} nm 700, 636 (sh), 430, 402 (sh), 328, 273, 255. ES-MS: m/z 1040 (MH^+). Anal. Calcd for $C_{76}H_{21}N_3O_4$: C, 87.77; H, 2.04; N, 4.04. Found: C, 82.70; H, 2.02; N, 3.77.

23. $C_{82}H_{33}N_3O_7$ (MW 1172.19), yield: 78% (69.0 mg, 0.06 mmol). Eluant: 99/1 toluene/iPrOH. IR-DRIFT: cm^{-1} 3274, 2933, 1649, 1120, 760, 530. ^1H NMR: δ 9.31 (bs, 1H), 7.56 (bs, 1H), 7.01 (s, 1H), 6.74 (s, 1H), 4.92 (d, $J = 10.0$ Hz, 1H), 4.65 (d, $J = 10.0$ Hz, 1H), 4.53 (m, 1H), 4.37 (m, 2H), 4.05 (s, 3H), 3.97−3.34 (m, 12H), 3.89 (s, 3H), 3.83 (s, 3H), 3.34 (s, 3H). ^{13}C NMR: δ 161.8, 155.6, 154.3, 153.4, 152.7, 149.9, 147.3, 147.2, 146.6, 146.3, 146.3, 146.2, 146.2, 146.1, 146.1, 146.0, 145.7, 145.6, 145.5, 145.4, 145.3, 145.3, 145.2, 145.2, 144.7, 144.5, 144.4, 144.4, 143.1, 143.1, 142.7, 142.7, 142.6, 142.2, 142.2, 142.1, 142.0, 141.8, 141.7, 140.3, 140.2, 140.0, 139.8, 139.6, 139.1, 136.9, 136.1, 136.1, 135.7, 131.1, 125.8, 123.4, 74.0, 73.6, 72.0, 70.8, 70.6, 70.5, 69.9, 61.6, 61.2, 59.1, 56.4, 50.1, 37.9, 29.8. UV−vis (cyclohexane): λ_{max} nm 255, 328, 402 (sh), 430, 458 (sh), 550 (sh), 636 (sh), 701. ES-MS: m/z 1172 (MH^+). Anal. Calcd for $C_{82}H_{33}N_3O_7$: C, 84.02; H, 2.84; N, 3.58. Found: C, 79.80; H, 2.89; N, 3.33.

24. $C_{79}H_{27}N_3O_4$ (MW 1082.11), yield: 60% (51.8 mg, 0.05 mmol). Eluant: 99/1 toluene/iPrOH. IR-DRIFT: cm^{-1} 3265, 2880, 1640, 1115, 527. ^1H NMR: δ 9.46 (bs, 1H), 7.70 (bt, 1H), 7.54 (d, $J = 7.0$ Hz, 1H), 7.39 (d, $J = 8.4$ Hz, 1H), 7.20 (t, $J = 8.4$ Hz, 1H), 7.04 (t, $J = 7.0$ Hz, 2H), 4.89 (d, $J = 9.9$ Hz, 1H), 4.65 (dd, $J = 10.2$ and 2.9 Hz, 1H), 4.54 (dd, $J = 8.9$ and 2.9 Hz, 1H), 4.38 (m, 1H), 4.34 (d, $J = 9.5$ Hz, 1H), 4.18−3.38 (m, 12H), 3.38 (s, 3H). ^{13}C NMR: δ 161.9, 155.6, 154.3, 152.7, 146.6, 146.2, 146.0, 145.6, 145.3, 143.2, 143.1, 142.7, 142.2, 142.2, 142.1, 141.8, 140.4, 140.0, 139.6, 136.9, 136.3, 136.1, 135.7, 131.3, 127.8, 124.4, 122.0, 120.6, 112.0, 74.8, 74.1, 73.5, 72.0, 70.9, 70.5, 69.9, 66.1, 66.0, 59.1, 50.1, 37.9. UV−vis (cyclohexane): λ_{max} nm 702, 540 (sh), 430, 405 (sh), 329, 302 (sh), 274, 253. ES-MS: 1082 (MH^+). Anal. Calcd for $C_{79}H_{27}N_3O_4$: C, 87.69; H, 2.52; N, 3.88. Found: C, 85.90; H, 2.58; N, 3.78.

25. $C_{73}H_{14}N_2O_2$ (MW 950.94), yield: 88% (66.9 mg, 0.07 mmol). Eluant: 99/1 toluene/iPrOH . IR-DRIFT: cm^{-1} 2920, 2805, 1671, 1595, 1504, 1341, 1178, 747. ^1H NMR (3/1 $CDCl_3/CS_2$): δ 7.79 (bt, 1H), 7.66 (m, 1H), 7.53 (m, 2H) 7.38 (m, 1H), 7.27 (m, 1H), 4.55 (s, 4H), 4.03 (m, 2H), 3.45 (t, $J = 6.0$ Hz, 2H). ^{13}C NMR (3/1 $CDCl_3/CS_2$): δ 158.7, 154.5, 154.4, 148.7, 147.2, 146.1, 145.9, 145.8, 145.4, 145.1, 144.4, 143.0, 142.5, 142.0, 141.9, 141.7, 140.1, 136.1, 127.5, 126.9, 123.6, 122.7, 111.7, 110.4, 70.5, 67.1, 52.3, 37.5. UV−vis (cyclohexane): λ_{max} nm 702, 465 (sh), 432, 328, 305, 255, 209. ES-MS: m/z 951 (MH^+). Anal. Calcd for $C_{73}H_{14}N_2O_2$: C, 92.21; H, 1.48; N, 2.95. Found: C, 88.90; H, 1.76; N, 2.69.

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Supporting Information Available: ^1H and ^{13}C or ES-MS spectra for compounds **8a**, **8c**, **9a**, **9c**, **10**, **13**−**15**, **17**, **18**, and **22**−**25**. This material is available free of charge via the Internet at http://pubs.acs.org.

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