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Sequential Copper-Catalyzed Alkyne–Azide Cycloaddition and Thiol-Maleimide Addition for the Synthesis of Photo- and/or Electroactive Fullerodendrimers and Cysteine-Functionalized Fullerene Derivatives

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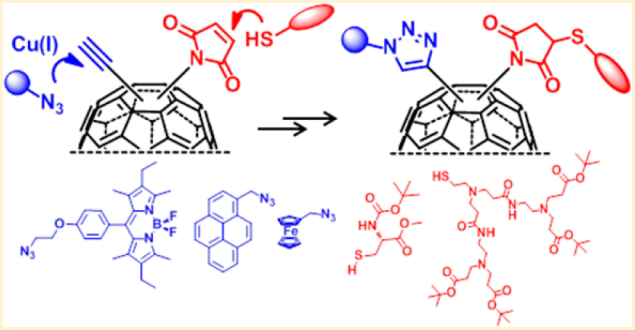
Supporting Information

ABSTRACT: In this study, the functionalization of a fullerene building block in a stepwise process by means of the copper-catalyzed alkyne–azide cycloaddition (CuAAC) and thiol-maleimide reactions is reported. Grafting of the fullerene platform with a variety of azido derivatives, including Bodipy, pyrene and ferrocene, was carried out first. These fullerene compounds were then reacted with thiol derivatives to yield sophisticated structures comprising photo- and/or electroactive fullerodendrimers and cysteine-functionalized fullerene assemblies. This strategy, which combines the CuAAC and thiol-maleimide processes, could become more widely adopted in the field of fullerene chemistry.



INTRODUCTION

Fullerene [60] derivatives have found many promising applications in material[1] and life sciences.[2] The chemical functionalization of fullerene is required to overcome the solubility problems encountered with C_{60} that limit its use in many applications. This functionalization has also been considered in order to develop sophisticated molecular structures such as donor–acceptor systems.[1d,3] Fullerene derivatives are mainly prepared by direct functionalization of C_{60} in the final step of a given synthesis. Conversely, the postfunctionalization route that consists of the derivatization of a fullerene building block has been less studied. This is due to the electron-deficient polyene nature of the C_{60} core, that limits the range of available reactions to cleanly functionalize fullerene derivatives. Nevertheless, a number of reactions including esterification,[4] amidification,[5] condensation[6] and copper-catalyzed alkyne–azide cycloadditions (CuAAC) have been reported.[7] Among these reactions, CuAAC appears as a very powerful synthetic tool for the functionalization of fullerene building blocks. The CuAAC reaction, which is at the forefront of the click chemistry concept developed by Sharpless and co-workers,[8] displays interesting features including high regioselectivity, high efficiency, high functional group tolerance and compatibility with a wide range of solvents. As a consequence, this reaction has been implemented in fullerene chemistry and has allowed the synthesis of a huge number of fullerene derivatives including photoactive-C_{60} conjugates,[9] photo- and electroactive fullerene hexa-adducts,[10] fullerene sugar balls,[11] fullerodendrimers,[12] C_{60}-functionalized polymers,[7b,13] C_{60}-viral nanoparticle conjugates,[14] protein-coated nanocapsules[15] and supramolecular fullerene motifs.[16] The success of the CuAAC reaction in fullerene chemistry has prompted us and others to evaluate other reactions that display some features of click chemistry. Among these reactions, Diels–Alder cyclo-additions, radical and nucleophilic additions (based on primary amines as a source of nucleophile) can be excluded due to the chemical reactivity of the fullerene core. Nierengarten and co-workers have described the synthesis of a fullerene derivative bearing three different groups: TMS-protected alkyne, azide and methyl acrylate units that can be functionalized in sequential CuAAC and thiol–ene click reactions.[17] In this example, the use of a hexa-adduct along with reactive methacrylate units was critically essential to favor addition of thiyl radicals to the methacrylate units instead of addition to the fullerene core. We recently reported a different strategy based on orthogonal functionalization of a fullerene monoadduct through the CuAAC and the thiol-maleimide reactions.[18] The latter attracted our attention given its reliability, efficiency and

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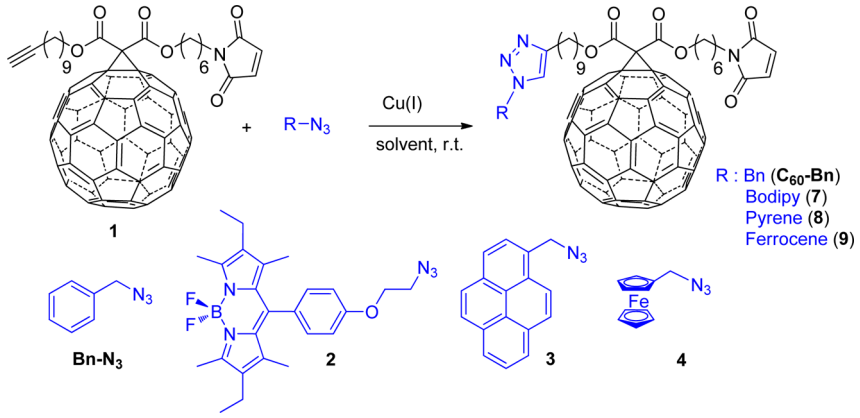
Table 1. Results for the CuAAC Reaction of Fullerene Derivative 1 with Azido Derivatives



entry	reactant (equiv)	source of Cu(I)	solvent	time (h)	product	yield (%)[a]
1	**Bn-N$_3$** (1.1)	CuSO$_4$/NaAsc (1/2)[b]	CH$_2$Cl$_2$/H$_2$O (1/1)	6	**C$_{60}$-Bn**	72
2	**2** (1.1)	CuSO$_4$/NaAsc (1/2)[b]	CH$_2$Cl$_2$/H$_2$O (1/1)	5	**7**	55
3	**3** (1.5)	CuSO$_4$/NaAsc (1.5/3)[b]	CH$_2$Cl$_2$/H$_2$O (1/1)	24	**8**	47
4	**4** (1.3)	CuSO$_4$/NaAsc (1.5/3)[b]	CH$_2$Cl$_2$/H$_2$O (1/1)	29	**9**	42
5	**Bn-N$_3$** (1.1)	CuBr/DIPEA (1/1)[c]	CH$_2$Cl$_2$	5	**C$_{60}$-Bn**	80
6	**2** (1.1)	CuBr/DIPEA (1/1)[c]	CH$_2$Cl$_2$	5	**7**	89
7	**3** (1.1)	CuBr/DIPEA (1.5/1.5)[c]	CH$_2$Cl$_2$	29	**8**	55
8	**4** (1.1)	CuBr/DIPEA (1.5/1)[c]	CH$_2$Cl$_2$	18	**9**	53

[a]Isolated yields after column chromatography. [b]In bracket: number of equivalent of copper sulfate (CuSO$_4$) and sodium ascorbate (NaAsc) [c]In bracket: number of equivalent of copper bromide (CuBr) and *N*,*N*-diisopropylethylamine (DIPEA)

selectivity. As such, the thiol-maleimide reaction has been developed extensively in bioconjugations[19] and more recently in polymer and materials synthesis.[20] The choice of the monoadduct fullerene building block was made to retain most of the properties of pristine C$_{60}$. This derivative, that possesses on one side an alkyne unit and on the other side a maleimide moiety, was easily functionalized in a model reaction by sequential orthogonal transformations with benzyl azide and 1-octanethiol.[18] In order to further demonstrate the relevance of our strategy, we report in this work a series of functionalized fullerene derivatives including photoactive, electroactive, dendritic and cysteine moieties. A set of azido and thiol derivatives was employed for the functionalization of the fullerene platform. These derivatives were chosen in connection with the properties they can provide to complement fullerene C$_{60}$. As far as the azido compounds were concerned, we focused our study on three derivatives, including Bodipy, pyrene and ferrocene. Boron dipyrin (Bodipy) is a well-known organic photosensitizer that leads to photoinduced energy or electron transfer when it is associated with fullerene C$_{60}$. Depending on the nature of the photoinduced process, C$_{60}$-Bodipy assemblies can be used either as organic triplet photosensitizers for triplet−triplet annihilation up-conversion[16c,21] and photocatalysis[22] applications or in artificial photosynthesis systems[23] for solar energy and fuel productions. Pyrene derivatives are interesting anchors that can be used to associate fullerene with other carbon nanostructures such as graphene[24] and nanotubes[25] through $\pi-\pi$ stacking interactions. The resulting carbon based supramolecular structures may be useful as materials in optoelectronic devices. Ferrocene is a well-known electron donor that has been associated with fullerene C$_{60}$. The ferrocene-fullerene dyads obtained represent a good model to investigate electron transfer processes from a fundamental point of view.[26] As far as the thiols were concerned, we chose to focus our study on dendrimers and cysteine moieties. The former was used as hydrophilic addends to obtain fullerodendrimers that may be soluble in water or physiological media for biological applications.[27] In addition, fullerodendrimers have also been developed for materials science applications.[12c,28] Finally, the cysteine moiety has been used as a means to label specifically proteins for target detection, quantification and analyses.[29] We think that the use of the thiol-maleimide reaction may be useful to incorporate fullerene derivatives into biological systems.

RESULTS AND DISCUSSION

We began our study by the functionalization of our fullerene building block (**1**) with azido derivatives (**2**−**4**) through the CuAAC reaction (Table 1). Among the variety of different source of copper(I) that has been described to perform this reaction,[30] we focused on the use of copper sulfate with sodium ascorbate (NaAsc) as the reducing agent. This procedure is convenient from a practical point of view, since the reaction can be performed in the presence of water, most commonly in a water/alcohol mixture, without the need for ligands or additives and has the advantage of not requiring an inert atmosphere. For these reasons, the "aqueous CuSO$_4$/sodium ascorbate" procedure is probably the most commonly used click protocol reported in the literature. Nierengarten and co-workers were the first to describe the use of this catalyst to functionalize a set of fullerene-alkyne derivatives with benzyl azide in a mixture of dichloromethane and water under vigorous stirring, dichloromethane being necessary to solubilize the fullerene-alkyne derivatives.[7c] In our previous report, the conditions described by Nierengarten and co-workers were used with our fullerene building block **1**. Optimized conditions were found using an equimolar amount of copper sulfate with a 2-fold excess of sodium ascorbate, in combination with a slight excess of benzyl azide, in a mixture of CH$_2$Cl$_2$/H$_2$O under vigorous stirring at room temperature.[18] The functionalization of **1** with azido derivatives **2**−**4** was first investigated using this system. The

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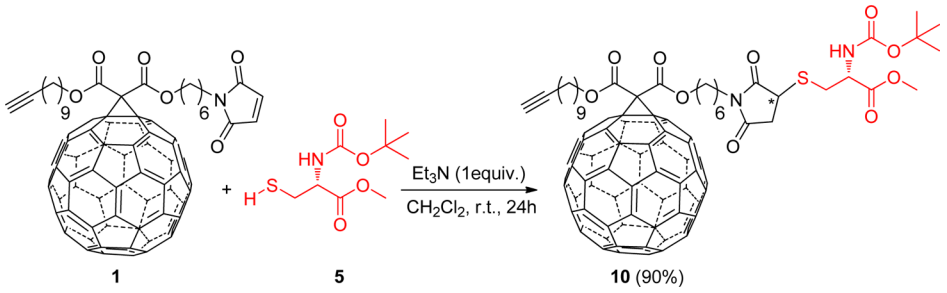
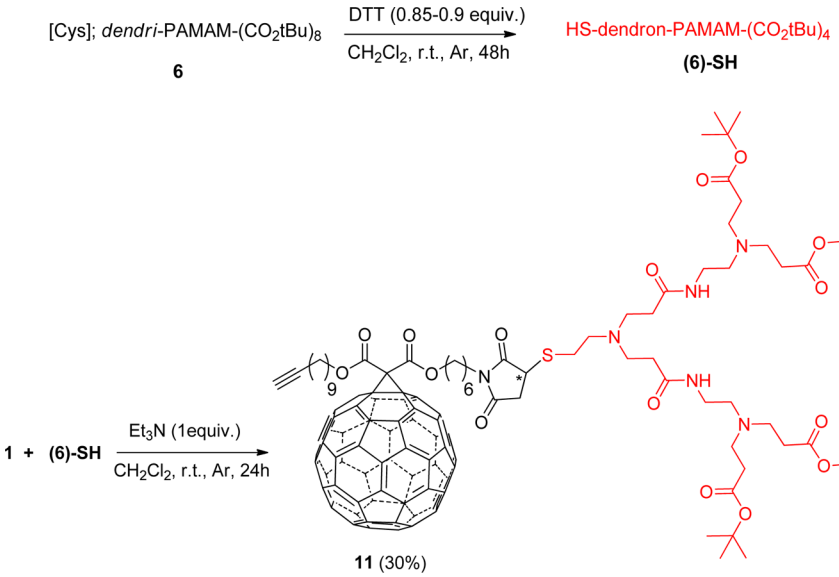
Scheme 1. Thiol-Maleimide Reaction between the Fullerene Platform 1 and *N*-(*tert*-Butoxycarbonyl)-L-cysteine Methyl Ester 5



1 **5** **10** (90%)

Scheme 2. Thiol-Maleimide Reaction between the Fullerene Platform 1 and the Sulphydryl-Functionalized Poly(amidoamine) PAMAM Dendron (6)-SH



6 **(6)-SH** **11** (30%)

ratios of $CuSO_4$/NaAsc were adjusted for each derivative to optimize the yields of the reactions.

The conversions of the platform, monitored by TLC analysis, were not complete after several hours, except in the case of Bodipy **2** (Table 1, entry 2). The addition of a second portion of the source of Cu(I) and prolonged reactions times were required for **3** and **4** (Table 1, entries 3−4) for the reaction to reach completion. The yields of these reactions varied from 42 to 55% for derivatives **9** to **7**, respectively, and are lower than the 72% yield obtained with benzyl azide (**Bn-N$_3$**). This prompted us to investigate other conditions,[7e] and to focus on the use of copper(I) bromide as the copper source in the presence of *N*,*N*-diisopropylethylamine as an additive (DIPEA) in oxygen-free conditions.[30] This system was first investigated by reacting **1** with benzyl azide, a reaction that has been used by us and others as a benchmark to study the reactivity of fullerene-alkyne derivatives (vide supra). The reaction was performed in dichloromethane using an equimolar amount of copper(I) bromide and a slight excess of benzyl azide (1.1 equiv). The resulting cycloadduct (**C$_{60}$-Bn**) was obtained in very good yield (80%; entry 5 Table 1). With these conditions in hand, the reaction was then conducted with azides **2**−**4**. As previously observed with copper sulfate, the reaction was complete within several hours with the azido derivative **2**, while prolonged reaction times as well as an excess of copper bromide were required with **3** and **4**. The overall yields of the reaction increased (up to 89% for **7**; entry 6 Table 1) using this system but remained moderate (53−55%) with pyrene-azide and ferrocene-azide. For these substrates, we observed the formation of an insoluble black solid that could be attributed to the formation of oligomeric copper acetylides. The slow reaction rate observed between these azides (**3**, **4**) and the alkyne (**1**) could favor the formation of these oligomeric species which partially consume the starting material. These oligomeric derivatives once formed are unable to react with azides (which could explain the moderate yields obtained for **8** and **9**).[31] Compounds **7**−**9** were fully characterized by ^{1}H and ^{13}C NMR spectroscopy and by electrospray mass spectrometry; the data were in accordance with the depicted structures. Inspections of their ^{1}H NMR spectra clearly indicate the typical singlet corresponding to the triazole unit and the signal of the CH_2−triazole protons. Importantly, the peak corresponding to the maleimide unit was retained. Finally, the signals corresponding to the protons of the azido derivatives (Bodipy, pyrene and ferrocene) were also observed (see Supporting Information for the structural assignments of **7**−**9**).

The thiol-maleimide Michael addition of the fullerene platform **1** with thiol derivatives was then studied. We first focused on the *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester **5** to assess the reactivity between the maleimide group of **1** and the thiol of this cysteine derivative (Scheme 1). The latter was used not only for solubility requirements, **5** being soluble in organic solvents while unprotected cysteine is not, but also because its protected *N*-Boc form prevents side reactions between the amine and the maleimide unit[32] or the C_{60} core. The reaction between **5**

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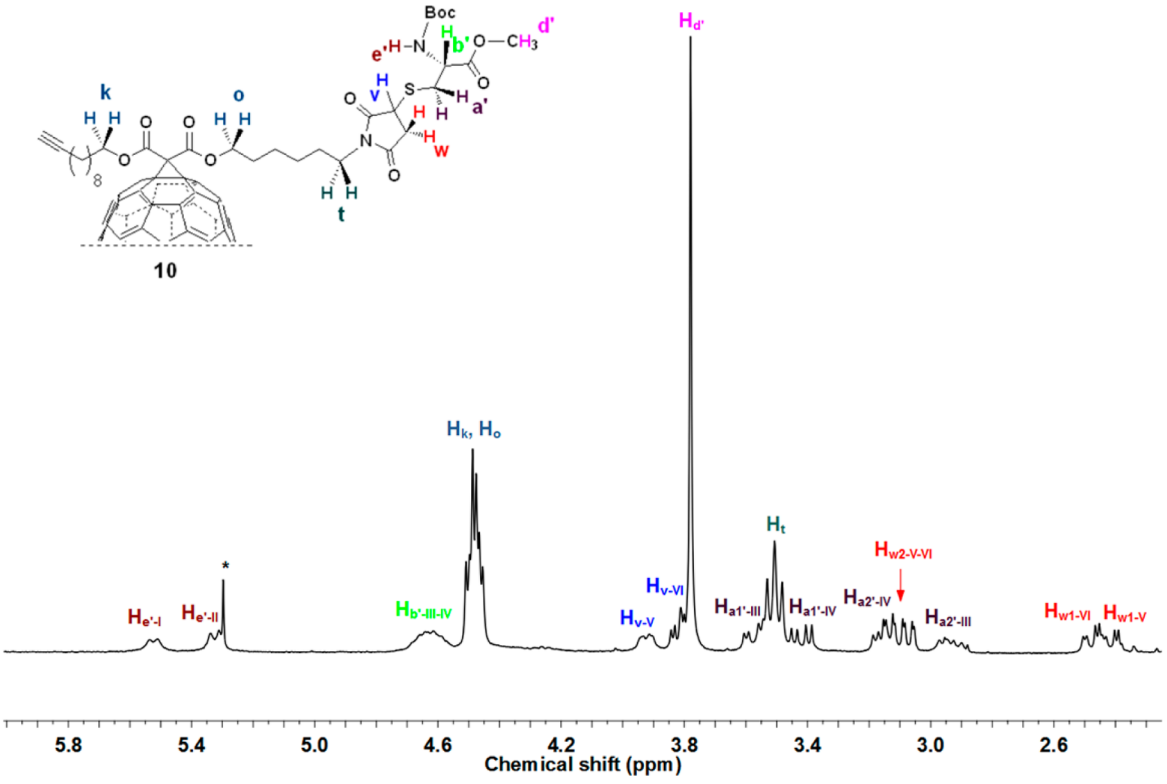

Figure 1. ^{1}H NMR spectrum recorded (300 MHz, $CDCl_3$, 25 °C) for the cysteine-functionalized fullerene derivative **10** in the 2.3−5.8 ppm region. The peak labeled with an asterisk is due to residual CH_2Cl_2.

and **1** was performed in dichloromethane in the presence of 1 equiv of triethylamine as base. The cysteine-functionalized fullerene derivative **10** was isolated after chromatographic separation on silica gel in high yield (90%).

The grafting of a mercapto-functionalized poly(amidoamine) PAMAM dendron (**6**)-**SH** onto the maleimide unit of the fullerene platform **1** was also considered (Scheme 2). The synthesis of PAMAM fullerodendrimers has already been described by direct functionalization of C_{60}.[33] We consider this approach (Scheme 2) as an alternative route that avoids the synthesis of unsymmetrical dendritic malonate precursors and their subsequent reaction with C_{60}. The reaction between the maleimide and the sulfhydryl-functionalized PAMAM dendron has already been used for the functionalization of peptides and for the surface modification of magnetic nanoparticles (MNPs) and of self-assembled monolayers (SAMs).[34] The cystamine-core PAMAM dendrimer [Cys]; dendri-PAMAM-$(CO_2tbu)_8$ **6** was first prepared using the method described by Tomalia and co-workers.[35] The mercapto-functionalized PAMAM Dendron (**6**)-**SH** was then produced in situ by reduction of the disulfide function found in cystamine-core PAMAM dendrimer **6** using dithiothreitol (DTT) as a reducing agent, and was used without further purification. The reaction of the maleimide-functionalized fullerene derivative **1** and the mercapto-functionalized PAMAM derivative (**6**)-**SH** was then realized in CH_2Cl_2 in the presence of triethylamine. Fullerodendrimer **11** was isolated after chromatographic separation using first silica gel, then gel permeation, in 30% yield. A small quantity relative to that of the isolated fullerodendrimer **11** of a byproduct was also isolated during the gel permeation chromatography. This derivative, that was eluted first during the gel permeation chromatography, displayed a brown color in solution and could result from the addition of the sulfhydryl-functionalized dendron onto the C_{60} core of **1**.

The structures of fullerene derivatives **10** and **11** were confirmed by a combination of ^{1}H and ^{13}C NMR, and electrospray mass spectrometry analyses. Their ^{1}H NMR spectra show the disappearance of the maleimide proton at 6.68 ppm while the signal corresponding to the alkyne moiety is still present at 1.93 ppm. Importantly, the formation of the thiol-maleimide adduct was also confirmed by the detection of a set of new signals in addition to the signals corresponding to the cysteine and PAMAM moieties. The cysteine-functionalized fullerene derivative **10** was obtained as a mixture of two diastereoisomers (Figure 1). Thus, two sets of seven NMR signals corresponding to the protons of the cysteine-maleimide unit ($\mathbf{H_a}'$, $\mathbf{H_b}'$, $\mathbf{H_e}'$, $\mathbf{H_v}$ and $\mathbf{H_w}$) are observed in the 2.3−5.7 ppm region. Proton $\mathbf{H_e}'$ displays two doublets located at 5.54 and 5.34, while proton $\mathbf{H_v}$ gives a broad doublet and a doublet of doublet at 3.92 and 3.82 ppm, respectively. The methylenic protons $\mathbf{H_a}'$ and $\mathbf{H_w}$ close to the chiral centers $\mathbf{C_b}'$ and $\mathbf{C_v}$, respectively, are diastereotopic and show a set of AB patterns. As far as the fullerodendrimer **11** is concerned, inspection of its ^{1}H NMR spectrum indicates the expected features of the PAMAM Dendron and the thiol-maleimide adduct. Proton $\mathbf{H_v}$ displays one signal at 3.80 ppm, the diastereotopic methylenic protons $\mathbf{H_w}$ give rise to an AB pattern, while the signal of $\mathbf{H_a}'$ is hidden behind the signal of the N−CH_2 protons of the PAMAM.

Finally, the utility of the fullerene building block **1** was further demonstrated by combining the CuAAC and the thiol-maleimide reactions using a sequential orthogonal transformation (Scheme 3). As previously reported in a model reaction, the best results were obtained when the CuAAC reaction was performed first, then the thiol-maleimide Michael addition.[18] Consequently, the triazole-linked Bodipy- (**7**), pyrene- (**8**) and ferrocene- (**9**)

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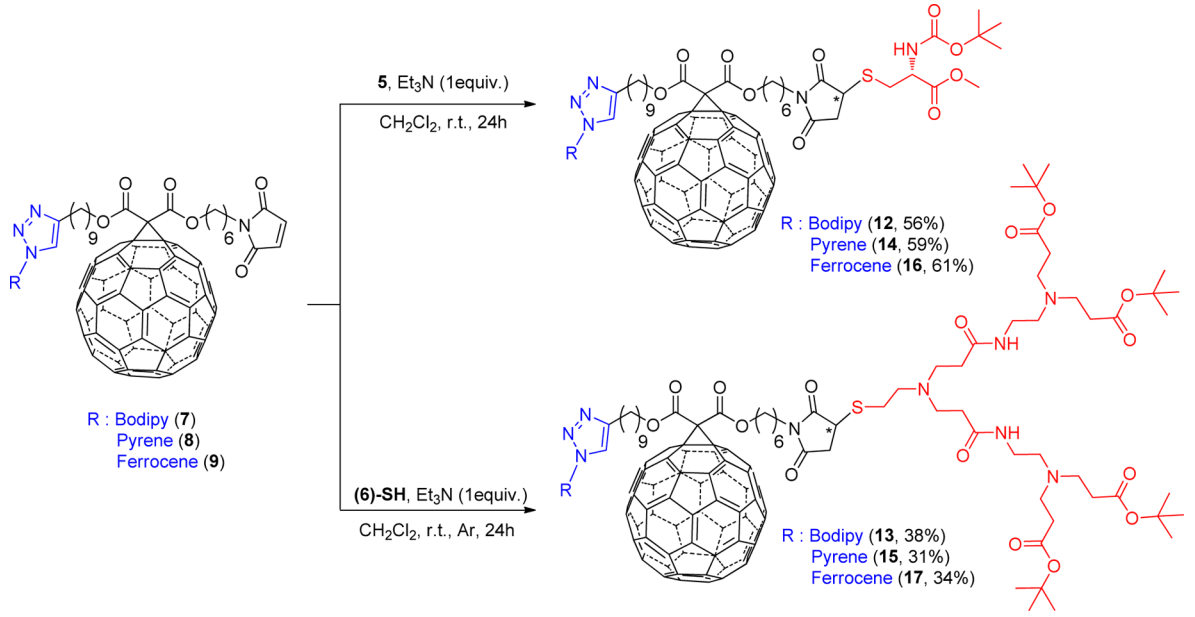
Scheme 3. Thiol-Maleimide Reaction between the Triazole-Linked Fullerene Derivatives (7−9) and the Thiols Derivatives (5 and (6)-SH)



fullerene derivatives were subjected to the thiol-maleimide reactions with the *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester (**5**) and the sulphydryl-functionalized PAMAM dendron (**6**)-**SH** using the same conditions as above. A set of six new adducts was isolated namely Bodipy/cysteine- (**12**), Bodipy/PAMAM- (**13**), pyrene/cysteine- (**14**), pyrene/PAMAM- (**15**), ferrocene/cysteine- (**16**) and ferrocene/PAMAM- (**17**) fullerene derivatives. The yields of the reactions followed the same trend as previously observed, the cysteine addition leading to relatively good yields (56−61%) while the PAMAM addition gave only moderate yields (31−38%). The structures of all fullerene derivatives (**12**−**17**) were confirmed by a combination of ^{1}H and ^{13}C NMR, and electrospray mass analyses. The NMR spectra display the expected features of the triazole and the cysteine-maleimide units along with the NMR signals of each moiety.

The association of photoactive and electroactive moieties on the fullerene derivatives prompted us to study their steady-state electronic and electrochemical properties. Electronic absorption spectra of the Bodipy-fullerene dyads (**12**, **13**) and reference compound (**2**) were recorded in dichloromethane (Figure 2a). The absorption band at 327 nm displayed in the spectra of the dyads (**12**, **13**) was ascribed to fullerene absorption. The sharp band located at 426 nm characteristic of [6,6]-methanofullerene derivatives was also observed. The strong absorption band of the Bodipy unit corresponding to the $S_0 \rightarrow S_1$ transition was observed at 525 nm for **2** and 526 nm for the dyads (**12**,**13**), respectively.

Electronic absorption spectra of the pyrene-fullerene dyads (**14**, **15**) and references compounds (**3** and the methanofullerene **Full-ref**, see the Supporting Information for the structure) were also recorded in dichloromethane (Figure 2b). All compounds containing the pyrene unit exhibit the typical absorption peaks in the 300−350 nm range that correspond to the pyrene $S_0 \rightarrow S_2$ transition. These peaks are located at 316, 329, and 346 nm for **3**, and 328 and 345 nm for the dyads (**14**, **15**), respectively. The band at 328 nm for the dyads is much higher in intensity due to overlap with the fullerene absorption band. The absorption bands observed in the 400−700 nm range are ascribed to fullerene absorption with the sharp peak at 426 nm and the peak at 690 nm corresponding to the fullerene $S_0 \rightarrow S_1$ transition. The typical broad band of methanofullerene which is centered around 480 nm is also observed.[36] As far as the ferrocene-fullerene dyads are concerned, they display the same features with the typical absorption bands located at 326, 426, and 690 nm along with the broad band at 480 nm (Figure 2c).

Fluorescence emission spectra of the fullerene dyads containing the Bodipy (**12**, **13**) or the pyrene (**14**, **15**) units along with the reference derivatives (**2**, **3**) were recorded in dichloromethane (Figure 3a and 3b). Excitation of the Bodipy reference (**2**) at 495 nm leads to a strong emissive band at 536 nm while excitation of the pyrene reference (**3**) at 343 nm reveals emission bands in the 370−450 nm range corresponding to the pyrene monomer emission. As expected, fluorescence emissions are almost quantitatively quenched in all the dyads (**12**−**15**) with residual emission located at 538 nm or in the 370−450 nm range for bodipy- and pyrene-fullerene dyads, respectively. These quenching processes can be attributed to photoinduced events based on energy and/or electron transfer from the photoexcited state of photosensitizers (Bodipy or pyrene) to the fullerene C_{60}.

The electrochemical properties of ferrocene-functionalized fullerene derivatives **16** and **17** have been studied by cyclic voltammetry (CV) and their half-wave potentials vs ferrocene used as an internal reference are reported in Table 2. The cyclic voltammograms of these compounds are presented in Figure 4 and display two reversible fullerene-based reductions along with a reversible oxidation wave corresponding to the ferrocene unit. The reduction potentials are shifted to more negative values than that of pristine C_{60} due to the loss of a carbon−carbon double bond. Furthermore, these reduction waves are close to those of methanofullerene derivatives previously reported in the literature.[37] It means that the presence of the ferrocene has a negligible effect on the first and second reduction waves of the fullerene cage.

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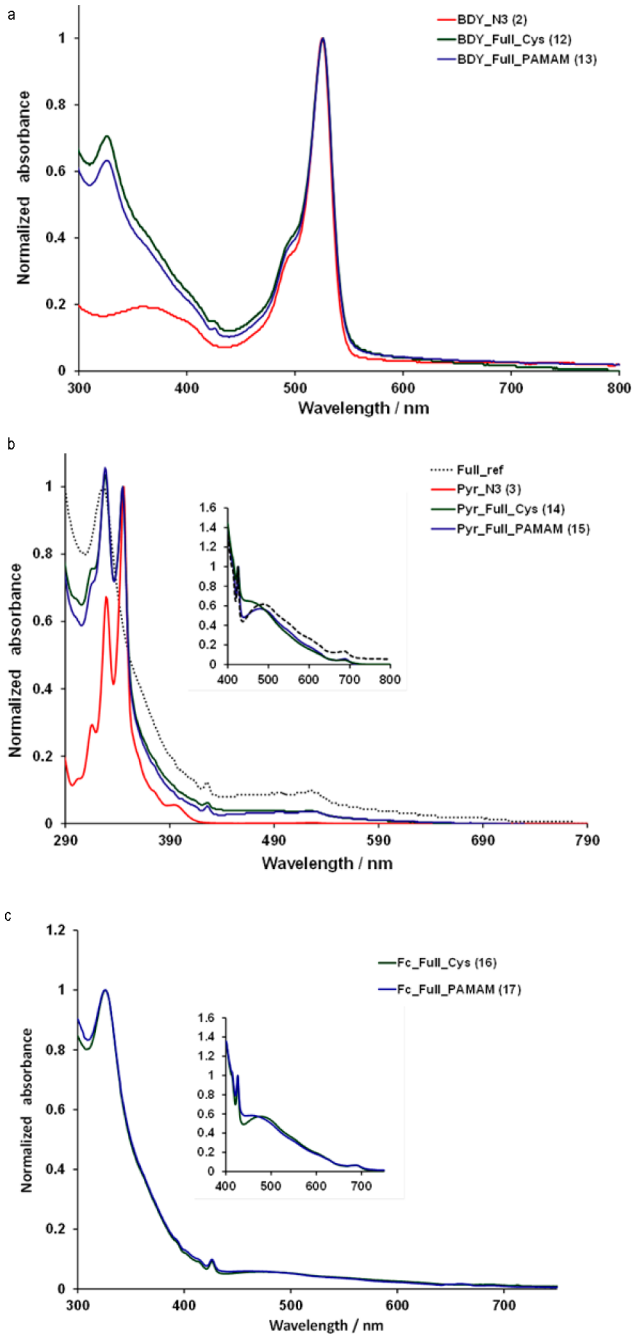

Figure 2. (a) Normalized absorption spectra (to the 525 nm band of Bodipy) of azido-Bodipy (**2**, [C] = 3.4 μM) and Bodipy-fullerene dyads (**12**, [C] = 3.5 μM and **13**, [C] = 5.1 μM) in dichloromethane. (b) Normalized absorption spectra (to the 345 nm band of pyrene, except for **Full-ref**) of methanofullerene (**Full-ref**, [C] = 6 μM), azidomethyl pyrene (**3**, [C] = 54.4 μM) and pyrene-fullerene dyads (**14**, [C] = 6.7 μM and **15**, [C] = 6.3 μM) in dichloromethane. The inset shows normalized absorption spectra (to the 426 nm band) from 400 and 800 nm in expanded form to visualize the fullerene absorption (concentrations are 20-fold higher). (c) Normalized absorption spectra (to the 326 nm band) of ferrocene-fullerene dyads (**16**, [C] = 7.1 μM and **17**, [C] = 5.4 μM) in dichloromethane. The inset shows normalized absorption spectra (to the 426 nm band) from 400 and 750 nm in expanded form to visualize the fullerene absorption (concentrations are 26-fold higher).

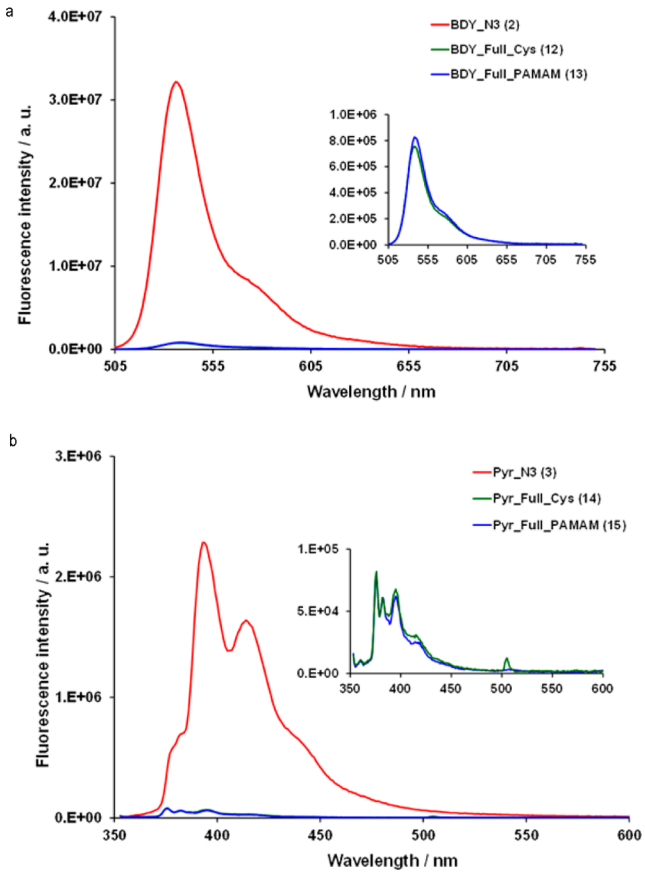

Figure 3. (a) Fluorescence spectra of azido-Bodipy (**2**, [C] = 0.34 μM) and Bodipy-fullerene dyads (**12**, [C] = 3.5 μM and **13**, [C] = 5.1 μM) in dichloromethane, $\lambda_{excitation}$ = 495 nm. The emission spectra were corrected for absorption at 495 nm. The 500−650 nm range is expanded for Bodipy-fullerene dyads to visualize the residual Bodipy emission. (b) Fluorescence spectra of azido methyl pyrene (**3**, [C] = 1.36 μM) and pyrene-fullerene dyads (**14**, [C] = 1.7 μM and **15**, [C] = 1.6 μM) in dichloromethane, $\lambda_{excitation}$ = 343 nm. The emission spectra were corrected for absorption at 343 nm. The 350−500 nm range is expanded for pyrene-fullerene dyads to visualize the residual pyrene emission.

Table 2. Half-Wave Potentials (V) of Fullerene Derivatives 16 and 17[a]

compound	$E^{1/2}_1$	$E^{1/2}_2$	$E^{1/2}_3$
16	0.091	−1.046	−1.428
17	0.092	−1.060	−1.447

[a]Versus ferrocene/ferrocenium. Experimental conditions: 0.9 mM of **16**, 0.6 mM of **17** and 0.1 mM of *n*-Bu_4NPF_6 in anhydrous and oxygen-free dichloromethane solution; pseudoreference electrode: Ag wire, working electrode: Pt, auxiliary electrode: Pt, scanning rate: 100 mV.s^{-1}.

CONCLUSION

In summary, we have prepared a series of functionalized fullerene derivatives through the use of copper-catalyzed alkyne−azide cycloaddition and thiol-maleimide reactions. Azido derivatives including Bodipy, ferrocene and pyrene were first grafted to our fullerene platform, which bears on one side an alkyne unit and a maleimide moiety on the other. A Copper(I) source based on $CuSO_4$/Na ascorbate in an aqueous−organic mixture or CuBr/DIEPA in an organic solvent was used for this reaction. The latter gave the best results with yields ranging from 53 to 89%. Triazole linked Bodipy, pyrene or ferrocene fullerene compounds were then functionalized by means of the thiol-maleimide reaction with cysteine derivative or sulphydryl-PAMAM Dendron. The former gave good yields close to 60%, while the yield of

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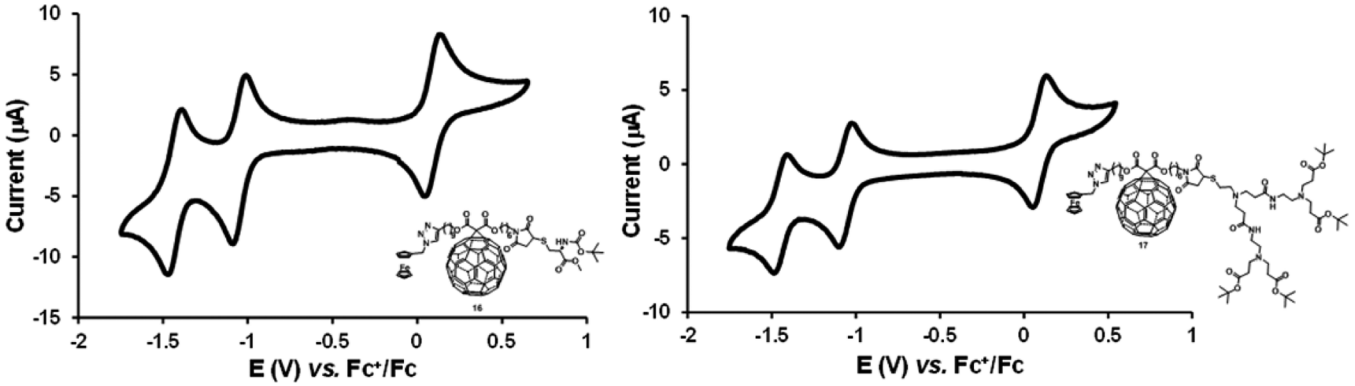
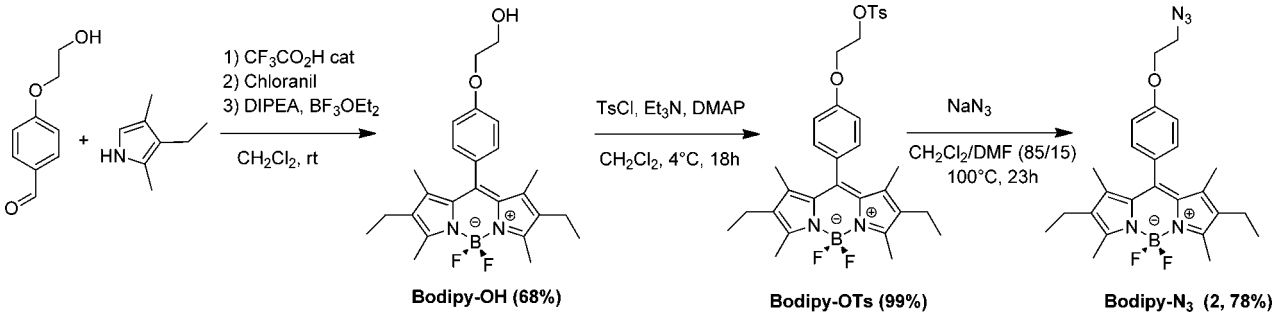


Figure 4. Cyclic voltammograms of the ferrocene-functionalized fullerenes **16** (on the left) and **17** (on the right).

Scheme 4. Synthetic Route for Azido-Bodipy 2



fullerodendrimer was only moderate. This work demonstrates that our fullerene building block can be tailored at will by combining the CuAAC and thiol-maleimide reactions, and could give an easy access to a wide range of highly desirable fullerene derivatives suitable for biological and materials applications. For instance, we wish to combine the features of photo and/or electroactive fullerene dyads with biological systems[38] thanks to the use of dendrimers or proteins via the cysteine labeling.

EXPERIMENTAL SECTIONS

General Methods. All reagents were used directly without further purification. The purity of fullerene C_{60} was 99.5+%. Dichloromethane (DCM) was dried and distilled over CaH_2 prior to use. Toluene was distilled over NaH prior to use. All other solvents were used as received. Column chromatography was performed using silica gel 60 (0.040−0.063 mm). Permeation gel chromatography was carried out with gel Bio-Beads SX1 (200−400 Mesh). Thin layer chromatography (TLC) was performed on aluminum sheets coated with silica gel 60 F_{254} and visualized by UV light. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz (^{1}H) and at 75.5 MHz (^{13}C) in $CDCl_3$. Chemical shifts (δ) were referenced to internal solvent $CDCl_3$ (7.26 for ^{1}H and 77.16 ppm for ^{13}C). High Resolution ESI-MS mass spectra were obtained with a Qtof analyzer type.

Cyclic Voltammetry. Ferrocene-functionalized fullerene derivatives **16** and **17** were dissolved in anhydrous dichloromethane containing 0,1 mM of *n*-Bu_4NPF_6 into a standard three-electrode cell under a nitrogen atmosphere. CV measurements were then undertaken with a potentiostat using a platinum disc electrode and a large platinum counter-electrode to obtain the potentials versus an Ag wire pseudoreference electrode. The latter was separated from the bulk solution using a capillary with frit. Potentials were calibrated versus ferrocene/ferrocenium.

Absorption and Fluorescence Analyses. Spectroscopic grade dichloromethane was used. Absorption spectra were recorded on a double-beam UV−visible spectrometer using a 10 mm path quartz cell. Fluorescence emission spectra were recorded on a fluorimeter. A right-angle configuration was used. Optical density of the samples was checked to be less than 0.1 to avoid reabsorption artifacts.

Synthesis of Compounds 1−4. Compounds **1**, **3** and **4** were prepared according to the procedures reported in the literature.[18,39,40] The azido-Bodipy **2** was prepared in three steps (Scheme 4) starting from the 4-(2-hydroxyethoxy) benzaldehyde using a modification of the synthetic route reported in the literature. The NMR data are in accordance with those reported in the literature.[41]

Synthesis of 6. A solution of [Cys]; *star*-PAMAM-$(NH_2)_4$ (2.0 g, 3.3 mmol) in methanol (30 mL) was introduced at 0 °C dropwise to a solution of *tert*-butyl acrylate (4.88 g, 38.4 mmol) in 10 mL of MeOH. The reaction mixture was stirred at room temperature for 48 h and concentrated under vacuum. The residue was purified by column chromatography (SiO_2, $CHCl_3$/MeOH: 85/15) to obtain a light yellow oil of [Cys]; *dendri*-PAMAM-$(CO_2tBu)_8$ **6** (4.70 g, 87%). ^{1}H NMR ($CDCl_3$) δ 7.16 (t, 4H, H_6, $^3J_{H-H}$ = 5.0 Hz); 3.30−3.24 (m, 8H, H_7); 2.83−2.70 (m, 32H, H_1−H_3, H_9); 2.53 (t, 8H, H_8, $^3J_{H-H}$ = 6.0 Hz); 2.36−2.31 (m, 24H, H_4, H_{10}); 1.43 (s, 72H, H_{13}) ppm. ^{13}C NMR ($CDCl_3$) δ 172.2, 172.1 (C_5, C_{11}); 80.6 (C_{12}); 52.7 (C_8); 52.6; 49.7; 49.4; 37.5 (C_7); 36.1; 33.8; 33.6; 28.2 (C_{13}) ppm. HRMS (ESI+) *m*/*z* calcd for $C_{80}H_{149}N_{10}O_{20}S_2$: 1634.0391 [M + H$^+$], found 1634.0402.

Synthesis of C_{60}-Bn. Compound **1** (30 mg, 26 μmol) and benzyl azide **Bn-N$_3$** (3.6 μL, 29 μmol) were dissolved in 3.5 mL of freshly distilled DCM. Argon was then bubbled through for 10 min. To this oxygen-free solution were added successively CuBr (3.8 mg, 26 μmol) and DIPEA (4.5 μL, 26 μmol). The reaction mixture was stirred at room temperature for 5 h under argon and then diluted with 15 mL of DCM. The mixture was washed with water (3 × 20 mL), the organic layer dried over anhydrous $MgSO_4$ and concentrated to dryness. Purification of the residue by column chromatography (SiO_2, DCM/Et_2O: 95/5) afforded 27 mg of **C_{60}-Bn** as a black solid in 80% yield. The NMR data are in accordance with those previously reported.[18]

Synthesis of 7. *Source of Cu(I)_CuSO$_4$/Sodium Ascorbate.* Compound **1** (60 mg, 52 μmol) and Bodipy-azide **2** (27 mg, 57 μmol) were dissolved in 2 mL of DCM. Then 2 mL of water, 8 mg of $CuSO_4$ (50 μmol), and 21 mg of sodium ascorbate (106 μmol) were added. The reaction mixture was stirred at room temperature for 5 h and then diluted with 15 mL of DCM. The mixture was washed with water

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(3 × 20 mL), the organic layer dried over anhydrous $MgSO_4$ and concentrated to dryness. Purification of the residue by column chromatography (SiO_2, DCM, then DCM/Et_2O: 95/5) afforded 46 mg of **7** as a black-red solid in 55% yield.

Source of Cu(I)_CuBr/DIEPA. Compound **1** (40 mg, 35 μmol) and Bodipy-azide **2** (18 mg, 37 μmol) were dissolved in 5 mL of freshly distilled DCM. Argon was then bubbled through for 10 min. To this oxygen-free solution were added successively CuBr (5 mg, 35 μmol) and DIPEA (6 μL, 35 μmol). The reaction mixture was stirred at room temperature for 5 h under argon and then diluted with 15 mL of DCM. The mixture was washed with an aqueous solution of EDTA (0.05M, 2 × 20 mL) and then with water (20 mL), the organic layer dried over anhydrous $MgSO_4$ and concentrated to dryness. Purification of the residue by column chromatography (SiO_2, DCM/Et_2O: 95/5) afforded 50 mg of **7** as a black-red solid in 89% yield. ^{1}H NMR ($CDCl_3$) δ 7.49 (s, 1H, H_a); 7.17 (d, 2H, H_5 or H_6, $^3J_{H-H}$ = 8.4 Hz); 6.97 (d, 2H, H_5 or H_6, $^3J_{H-H}$ = 8.4 Hz); 6.68 (s, 2H, H_v); 4.76 (t, 2H, H_7 or H_8, $^3J_{H-H}$ = 4.9 Hz); 4.50−4.45 (m, 4H, H_k, H_o); 4.41 (t, 2H, H_7 or H_8, $^3J_{H-H}$ = 4.9 Hz); 3.51 (t, 2H, H_u, $^3J_{H-H}$ = 7.2 Hz); 2.73 (t, 2H, H_c, $^3J_{H-H}$ = 7.7 Hz); 2.51 (s, 6H, H_4 or H_1); 2.29 (q, 4H, H_3, $^3J_{H-H}$ = 7.4 Hz); 1.87−1.78 (m, 4H, H_j, H_p); 1.70−1.55 (m, 4H, H_d, H_s); 1.52−1.25 (m, 20H, H_e-H_i, H_q-H_r, H_4 or H_1); 0.97 (t, 6H, H_2, $^3J_{H-H}$ = 7.4 Hz). ^{13}C NMR ($CDCl_3$) δ 171.0 (C_u); 163.8 (C_l, C_n); 158.4, 153.8 (Csp^2 Bodipy); 145.47, 145.45, 145.4, 145.3, 145.0, 144.79, 144.76, 144.73, 144.72, 144.0, 143.98, 143.2, 143.13, 143.11, 142.3, 142.0, 141.08, and 141.06 (Csp^2 C_{60}); 139.8 (Csp^2 Bodipy), 139.1 (Csp^2 C_{60}); 134.2 (C_v); 132.9, 131.2, 129.9, and 129.0 (Csp^2 Bodipy); 122.01 (C_a); 115.1 (Csp^2 Bodipy); 71.8 (Csp^3 C_{60}); 67.6, 67.3 (C_k, C_o); 66.7 (C_7 or C_8); 52.5 (C_m); 49.7 (C_7 or C_8); 37.8 (C_t) ; 29.64, 29.62, 29.5, 29.4, 29.3, 28.71, 28.65, 28.6, 26.5, 26.1, and 25.8 ($C_{d\text{-}j}$, $C_{p\text{-}s}$); 25.65 (C_c); 17.20 (C_3); 14.78 (C_2); 12.6, 12.0 (C_1, C_4) ppm. ^{19}F NMR ($CDCl_3$) δ −145.7 (q, 2F, $^1J_{F-B}$ = 32 Hz) ppm. ^{11}B NMR ($CDCl_3$) δ 1.97 (t, 1B, $^1J_{B-F}$ = 32 Hz) ppm. HRMS (ESI+) *m*/*z* calcd for $C_{109}H_{63}N_6O_7BF_2$: 1615.4856 [$M^{+\bullet}$], found 1615.4867.

Synthesis of 8. *Source of Cu(I)_CuSO$_4$/Sodium Ascorbate.* Compound **1** (60 mg, 52 μmol) and pyrene-azide **3** (20 mg, 77 μmol) were dissolved in 2 mL of DCM. Then 2 mL of water, 8 mg of $CuSO_4$ (50 μmol), and 21 mg of sodium ascorbate (106 μmol) were added. The reaction mixture was stirred at room temperature for 20 h. As TLC analysis revealed that **1** was not entirely consumed, 1 mL of water, 4 mg of $CuSO_4$ and 10 mg of sodium ascorbate were added again. The resulting mixture was allowed to stir at room temperature for 4 h and then diluted with 15 mL of DCM. The mixture was washed with water (3 × 20 mL), the organic layer dried over anhydrous $MgSO_4$ and concentrated to dryness. Purification of the residue by column chromatography (SiO_2, DCM, then DCM/Et_2O: 95/5) afforded 35 mg of **8** as a brown solid in 47% yield.

Source of Cu(I)_CuBr/DIEPA. Compound **1** (91 mg, 80 μmol) and pyrene-azide **3** (22 mg, 86 μmol) were dissolved in 8 mL of freshly distilled DCM. Argon was then bubbled through for 10 min. To this oxygen-free solution were added successively CuBr (12 mg, 84 μmol) and DIPEA (14 μL, 81 μmol). The reaction mixture was stirred at room temperature for 22 h under argon. As TLC analysis revealed that **1** was not entirely consumed, 6 mg of CuBr and 7 μL of DIPEA were added again. The resulting mixture was allowed to stir at room temperature for 7 h under argon and then was filtered to remove an insoluble black solid (oligomeric copper acetylides). The filtrate was diluted with 15 mL of DCM and was washed with an aqueous solution of EDTA (0.05M, 2 × 20 mL) and then with water (20 mL). The organic layer was finally dried over anhydrous $MgSO_4$ and concentrated to dryness. Purification of the residue by column chromatography (SiO_2, DCM/Et_2O: 95/5) afforded 60 mg of **8** as a brown solid in 55% yield. ^{1}H NMR ($CDCl_3$) δ 8.24−7.92 (m, 9H, −CH_{ar} Pyrene); 7.03 (s, 1H, H_a); 6.65 (s, 2H, H_v); 6.22 (s, 2H, −CH_2−Pyrene); 4.45 (t, 4H, H_k, H_o, $^3J_{H-H}$ = 6.4 Hz); 3.49 (t, 2H, H_u $^3J_{H-H}$ = 7.1 Hz); 2.59 (t, 2H, H_c, $^3J_{H-H}$ = 7.9 Hz); 1.85−1.72 (m, 4H, H_j, H_p); 1.63−1.22 (m, 18H, H_d-H_i, H_q-H_s) ppm. ^{13}C NMR ($CDCl_3$) δ 170.9 (C_u); 163.75, 163.74 (C_l, C_n); 148.9 (C_b), 145.43, 145.36, 145.27, 145.25, 145.20, 145.17, 144.9, 144.68, 144.65, 144.63, 143.90, 143.86, 143.11, 143.08, 143.01, 142.98, 142.2, 141.9, 140.99, 140.97, 139.06, and 139.0 (Csp^2 C_{60}); 134.1 (C_v); 132.2, 131.3, 130.7, and 129.4 (C_{ar}), 129.1, 128.4, 127.7, and 127.4 (CH_{ar}); 127.3 (C_{ar}); 126.5, 126.1, and 125.9 (CH_{ar}); 125.2 (C_{ar}); 125.1 (CH_{ar}); 124.7 (C_{ar}); 122.2 (CH_{ar}); 120.6 (C_a); 71.7 (Csp^3 C_{60}); 67.6, 67.3 (C_k, C_o); 52.5 (C_m); 52.4 ($\underline{C}H_2$ Pyrene); 37.8 (C_t); 29.5, 29.4, 29.33, 29.27, 29.2, 28.7, 28.6, 28.5, 26.5, 26.0, and 25.9 ($C_{d\text{-}j}$, $C_{p\text{-}s}$); 25.6 (C_c) ppm. HRMS (ESI+) *m*/*z* calcd for $C_{101}H_{45}N_4O_6$: 1409.3339 [M + H^+], found 1409.3352.

Synthesis of 9. *Source of Cu(I)_CuSO$_4$/Sodium Ascorbate.* Compound **1** (60 mg, 52 μmol) and ferrocene-azide **4** (19 mg, 79 μmol) were dissolved in 2 mL of DCM. Then 2 mL of water, 8 mg of $CuSO_4$ (50 μmol), and 21 mg of sodium ascorbate (106 μmol) were added. The reaction mixture was stirred at room temperature for 24 h. As TLC analysis revealed that **1** was not entirely consumed, 1 mL of water, 4 mg of $CuSO_4$ and 11 mg of sodium ascorbate were added again. The resulting mixture was allowed to stir at room temperature for 5 h and then diluted with 15 mL of DCM. The mixture was washed with water (3 × 20 mL), the organic layer dried over anhydrous $MgSO_4$ and concentrated to dryness. Purification of the residue by column chromatography (SiO_2, DCM then DCM/Et_2O: 95/5) afforded 30 mg of **9** as a brown solid in 42% yield.

Source of Cu(I)_CuBr/DIEPA. Compound **1** (71 mg, 61 μmol) and ferrocene-azide **4** (16 mg, 67 μmol) were dissolved in 10 mL of freshly distilled DCM. Argon was then bubbled through 10 min. To this oxygen-free solution were added successively CuBr (13 mg, 90 μmol) and DIPEA (10.5 μL, 61 μmol). The reaction mixture was stirred at room temperature for 18 h under argon and was then filtered to remove an insoluble black solid (oligomeric copper acetylides). The filtrate was diluted with 15 mL of DCM and was washed with an aqueous solution of EDTA (0.05M, 2 × 20 mL) and then with water (20 mL). The organic layer was finally dried over anhydrous $MgSO_4$ and concentrated to dryness. Purification of the residue by column chromatography (SiO_2, DCM/Et_2O: 95/5) afforded 45 mg of **9** as a brown solid in 53% yield. ^{1}H NMR ($CDCl_3$) δ 7.16 (s, 1H, H_a); 6.68 (s, 2H, H_v); 5.24 (s, 2H, $C\underline{H}_2$-Ferrocene); 4.49−4.45 (t, 4H, H_k, H_o, $^3J_{H-H}$ = 6.4 Hz); 4.26−4.16 (m, 9H, Ferrocene); 3.51 (t, 2H, H_u, $^3J_{H-H}$ = 7.2 Hz); 2.64 (t, 2H, H_c, $^3J_{H-H}$ = 7.6 Hz); 1.87−1.76 (m, 4H, H_j, H_p); 1.69−1.25 (m, 18H, H_d-H_i, H_q-H_s) ppm. ^{13}C NMR ($CDCl_3$) δ 170.9 (C_u), 163.8 (C_l, C_n); 145.47, 145.45, 145.37, 145.29, 144.8, 144.73, 144.71, 144.00, 143.98, 143.2, 143.12, 143.10, 142.3, 142.0, 141.1, and 139.1 (Csp^2 C_{60}); 134.2 (C_v); 120.0 (C_a); 81.3 ($C_{Ferrocene}$); 71.8 (Csp^3 C_{60}); 69.09 and 69.03 ($C_{Ferrocene}$); 67.6, 67.3 (C_k, C_o); 52.5 (C_m); 49.9 ($\underline{C}H_2$ Ferrocene); 37.8 (C_t); 29.8, 29.6, 29.4, 29.3, 28.7, 28.64, 28.56, 26.5, 26.1, and 25.9 ($C_{d\text{-}j}$, $C_{p\text{-}s}$); 25.7 (C_c) ppm. HRMS (ESI+) *m*/*z* calcd for $C_{95}H_{44}N_4O_6FeK$: 1431.2247 [M + K^+], found 1431.2286.

General Procedure for the Synthesis of Cysteine-Functionalized Fullerene Derivatives. *Synthesis of 10.* To a solution of compound **1** (60 mg, 52 μmol) in 2 mL of distilled DCM were added 22 μL of *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester (106 μmol) and 7 mL of triethylamine (50 μmol). The reaction mixture was stirred at room temperature for 24 h and concentrated to dryness. Column chromatography (SiO_2, DCM/Et_2O: 99/1 then 97/3) of the crude product afforded 65 mg of **10** as a black solid in 90% yield. ^{1}H NMR ($CDCl_3$) δ 5.53 (d, 1/2 H, $H_{e'\text{-}I}$, $^3J_{H-H}$ = 7.7 Hz); 5.33 (d, 1/2 H, $H_{e'\text{-}II}$, $^3J_{H-H}$ = 8.4 Hz); 4.70−4.56 (m, 1H, $H_{b'\text{-}III}$ and $H_{b'\text{-}IV}$); 4.50−4.45 (m, 4H, H_k, H_o); 3.93−3.91 (m, 1/2 H, $H_{v\text{-}V}$); 3.82 (dd, 1/2 H, $H_{v\text{-}VI}$); 3.77 (s, 3H, $H_{d'}$); 3.57 (dd, 1/2 H, $H_{a'1\text{-}III}$, $^3J_{H-H}$ = 4.3 Hz, $^2J_{H-H}$ = 14.0 Hz); 3.50 (t, 2H, H_u $^3J_{H-H}$ = 7.3 Hz); 3.41 (dd, 1/2 H, $H_{a'1\text{-}IV}$, $^3J_{H-H}$ = 5.7 Hz, $^2J_{H-H}$ = 14.1 Hz); 3.18−3.05 (m, 1/2 H, $H_{a'2\text{-}IV}$ and 1H, $H_{w2\text{-}V\text{-}VI}$); 2.93 (dd, 1/2 H, $H_{a'2\text{-}III}$); 2.48 (dd, 1/2 H, $H_{w1\text{-}VI}$); 2.41 (dd, 1/2 H, $H_{w1\text{-}V}$); 2,17 (dt, 2H, H_c, $^3J_{H-H}$ = 7.0 Hz, $^4J_{H-H}$= 2.6 Hz); 1,93 (t, 1H, H_a, $^4J_{H-H}$= 2.6 Hz); 1,87−1,78 (m, 4H, H_j, H_p); 1,61−1,24 (m, 18H, H_d-H_i, H_q-H_s); 1.44 (s, 9H, $H_{h'}$) ppm. ^{13}C NMR ($CDCl_3$) δ 176.7, 176.5, 174.5, 174.4, 171.4, and 163.8 (C = O); 145.43, 145.42, 145.35, 145.27, 145.26, 145.0, 144.8, 144.73, 144.71, 144.70, 144.0, 143.2, 143.10, 143.08, 142.3, 142.0, 141.05, 141.04, 139.07, and 139.06 (Csp^2 C_{60}); 84.9 (C_b); 80.5 ($C_{g'}$) ; 71.7 (Csp^3 C_{60}); 68.3 (C_a); 67.6, 67.3 (C_k, C_o); 52.93, 52.86 ($C_{b'\text{-}III\text{-}IV}$, $C_{d'}$); 52.5 (*Cm*); 39.05, 38.99, and 38.39 (C_u, $C_{v\text{-}V\text{-}VI}$); 36.1, 35.7, 34.8, and 34.2 ($C_{a'\text{-}III\text{-}IV}$, $C_{w\text{-}V\text{-}VI}$); 29.8, 29.6, 29.3, 29.2, 28.8, 28.7, 28.6, 28.5, 27.6, 26.4, 26.1, and 25.6 ($C_{d\text{-}j}$, $C_{p\text{-}s}$); 28.4 ($C_{h'}$) and 18.5 (C_c) ppm. HRMS (ESI+) *m*/*z* calcd for $C_{93}H_{50}N_2O_{10}SNa$: 1409.3084 [M + Na^+], found 1409.3101.

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Synthesis of ***12***. According to the general procedure, the reaction of **7** (50 mg, 30 μmol) with 13 μL of *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester (62 μmol) and 4 μL of triethylamine (29 μmol) in 3 mL of DCM for 17 h afforded 31 mg of **12** as a black-red solid in 56% yield after column chromatography (SiO_2, DCM/Et_2O: 90/10 then 85/15). ^1H NMR ($CDCl_3$) δ 7.49 (s, 1H, H_a); 7.17 (d, 2H, H_5 or H_6, $^3J_{H-H}$ = 8.2 Hz); 6.97 (d, 2H, H_5 or H_6, $^3J_{H-H}$ = 8.1 Hz); 5.54 (d, 1/2 H, $H_{e'\text{-I}}$, $^3J_{H-H}$ = 6.9 Hz); 5.34 (d, 1/2 H, $H_{e'\text{-II}}$, $^3J_{H-H}$ = 7.8 Hz); 4.77 (t, 2H, H_7 or H_8); 4.69−4.55 (m, 1H, $H_{b'\text{-III}}$ and $H_{b'\text{-IV}}$); 4.53−4.45 (m, 4H, H_k, H_o); 4.43−4.40 (m, 2H, H_7 or H_8); 3.93−3.91 (m, 1/2 H, $H_{v\text{-V}}$); 3.83 (dd, 1/2 H, $H_{v\text{-VI}}$, $^3J_{H-H}$ = 3.6 Hz, $^3J_{H-H}$ = 9.1 Hz); 3.77 (s, 3H, $H_{d'}$); 3.57 (dd, 1/2 H, $H_{a'1\text{-III}}$, $^3J_{H-H}$ = 4.4 Hz, $^2J_{H-H}$ = 14.3 Hz); 3.50 (t, 2H, H_υ, $^3J_{H-H}$ = 7.2 Hz); 3.42 (dd, 1/2 H, $H_{a'1\text{-IV}}$, $^3J_{H-H}$ = 5.6 Hz, $^2J_{H-H}$ = 14.2 Hz); 3.19−3.06 (m, 1/2 H, $H_{a'2\text{-IV}}$ and 1H, $H_{w2-V-VI}$); 2.94 (dd, 1/2 H, $H_{a'2\text{-III}}$); 2.73 (t, 2H, H_ω, $^3J_{H-H}$ = 7.5 Hz); 2.51 (s, 6H, H_4 or H_1); 2.49−2.39 (m, 1H, $H_{w1-V-VI}$); 2.29 (q, 4H, H_3); 1.89−1.76 (m, 4H, H_j, H_p); 1.75−1.54 (m, 4H, H_d, H_s); 1.53−1.14 (m, 20H, H_e-H_i, H_q-H_τ, H_4 or H_1); 1.45 (s, 9H, $H_{h'}$); 0.97 (t, 6H, H_2, $^3J_{H-H}$ = 7.5 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ 176.7, 176.5, 174.5, and 174.4 (C_υ, C_x, $C_{f'}$); 171.4 ($C_{c'}$); 163.8 (C_l, C_n); 158.5, 153.8 (Csp^2 Bodipy); 148.7 (C_b); 145.51, 145.46, 145.39, 145.38, 145.30, 145.29, 145.0, 144.8, 144.75, 144.73, 144.01, 143.99, 143.22, 143.20, 143.14, 143.10, 142.3, 142.0, 141.09, and 141.07 (Csp^2 C_{60}); 139.8 (Csp^2 Bodipy); 139.10, 139.07 (Csp^2 C_{60}); 138.4, 132.9, 131.2, 129.9 (C_5 or C_6) and 129.1 (Csp^2 Bodipy); 122.1 (Ca); 115.2 (C_5 or C_6); 80.5 ($C_{g'}$); 71.8 (Csp^3 C_{60}); 67.6, 67.3 (C_k, C_o); 66.7 (C_7 or C_8); 52.92, 52.85 ($C_{b'-III-IV}$, $C_{d'}$); 52.6 (C_m); 39.07, 39.02, and 38.5 (C_υ, C_{v-V-VI}); 36.1, 35.7, 34.4, and 34.3 ($C_{a'-III-IV}$, C_{w-V-VI}); 30.5, 29.63, 29.61, 29.46, 29.43, 28.7, 28.5, 27.6, 26.5, 26.1, and 25.8 (C_{d-j}, C_{p-s}); 28.4 ($C_{h'}$); 25.6 (C_c); 17.2 (C_3); 14.8 (C_2); 12.6, 12.0 (C_1, C_4) ppm. ^{19}F NMR ($CDCl_3$) δ −145.8 (q, 2F, $^1J_{F-B}$ = 32 Hz) ppm. ^{11}B NMR ($CDCl_3$) δ 1.97 (t, 1B, $^1J_{B-F}$ = 34 Hz) ppm. HRMS (ESI+) *m*/*z* calcd for $C_{118}H_{81}N_7O_{11}SBF_2$: 1851.5812 [M + H^+], found 1851.5824.

Synthesis of ***14***. According to the general procedure, the reaction of **8** (60 mg, 43 μmol) with 17.5 μL of *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester (85 μmol) and 6 μL of triethylamine (43 μmol) in 5 mL of DCM for 17 h afforded 41 mg of **14** as a black solid in 59% yield after column chromatography (SiO_2, DCM/Et_2O: 90/10 then 87/13). ^1H NMR ($CDCl_3$) δ 8.25−7.92 (m, 9H, $-CH_{ar}$ pyrene); 7.05 (s, 1H, H_a); 6.21 (s, 2H, $-CH_2-$Pyrene); 5.54 (d, 1/2 H, $H_{e'\text{-I}}$, $^3J_{H-H}$ = 7.6 Hz); 5.34 (d, 1/2 H, $H_{e'\text{-II}}$, $^3J_{H-H}$ = 8.0 Hz); 4.73−4.52 (m, 1H, $H_{b'\text{-III}}$ and $H_{b'\text{-IV}}$); 4.45 (t, 4H, H_k, H_o, $^3J_{H-H}$ = 6.4 Hz); 3.95−3.85 (m, 1/2 H, $H_{v\text{-V}}$); 3.81 (dd, 1/2 H, $H_{v\text{-VI}}$); 3.77 (s, 3H, $H_{d'}$); 3.56 (dd, 1/2 H, $H_{a'1\text{-III}}$); 3.48 (t, 2H, H_υ, $^3J_{H-H}$ = 7.3 Hz); 3.41 (dd, 1/2 H, $H_{a'1\text{-IV}}$, $^3J_{H-H}$ = 5.9 Hz, $^2J_{H-H}$ = 14.3 Hz); 3.18−3.03 (m, 1/2 H, $H_{a'2\text{-IV}}$ and 1H, $H_{w2-V-VI}$); 2.98−2.90 (m, 1/2 H, $H_{a'2\text{-III}}$); 2.59 (t, 2H, H_ω, $^3J_{H-H}$ = 7.7 Hz); 2.46 (dd, 1/2 H, $H_{w1\text{-VI}}$, $^2J_{H-H}$ = 11.0 Hz, $^3J_{H-H}$ = 3.3 Hz); 2.40 (dd, 1/2 H, $H_{w1\text{-V}}$, $^2J_{H-H}$ = 11.0 Hz, $^3J_{H-H}$ = 3.8 Hz); 1,85−1,71 (m, 4H, H_j, H_p); 1,65−1,21 (m, 18H, H_d-H_i, H_q-H_s); 1.44 (s, 9H, $H_{h'}$) ppm. ^{13}C NMR ($CDCl_3$) δ 176.7, 176.5, 174.5, and 174.4 (C_υ, C_x, $C_{f'}$); 171.4 ($C_{c'}$); 163.75, 163.73 (C_l, C_n); 148.9 (C_b); 145.5, 145.4, 145.31, 145.28, 145.2, 144.9, 144.72, 144.68, 144.65, 143.93, 143.89, 143.15, 143.12, 143.04, 143.01, 142.23, 142.21, 142.0, 141.02, 141.00, 139.1, and 139.0 (Csp^2 C_{60}); 132.2, 131.4, 130.8, and 129.5 (C_{ar}); 129.2, 128.4, 127.7, and 127.4 (CH_{ar}); 127.3 (C_{ar}); 126.6, 126.1, and 126.0 (CH_{ar}); 125.2 (C_{ar}); 125.1 (CH_{ar}); 124.7 (C_{ar}); 122.2 (CH_{ar}); 120.7 (C_a); 80.5 ($C_{g'}$); 71.8 (Csp^3 C_{60}); 67.6, 67.3 (C_k, C_o); 52.91, 52.84 ($C_{b'-III-IV}$, $C_{d'}$); 52.6 (C_m); 52.5 (CH_2 Pyrene); 39.09, 39.06, and 38.5 (C_υ, C_{v-V-VI}); 36.1, 35.7, and 34.3 ($C_{a'-III-IV}$, C_{w-V-VI}); 30.5, 29.8, 29.5, 29.4, 29.34, 29.27, 29.2, 28.7, 28.5, 27.6, 26.5, 25.8, and 25.6 (C_{d-j}, C_{p-s}); 28.4 ($C_{h'}$); 26.1 (C_c) ppm. HRMS (ESI+) *m*/*z* calcd for $C_{110}H_{61}N_5O_{10}SNa$: 1666.4037 [M + Na^+], found 1666.4034.

Synthesis of ***16***. According to the general procedure, the reaction of **9** (73 mg, 52 μmol) with 22 μL of *N*-(*tert*-butoxycarbonyl)-L-cysteine methyl ester (105 μmol) and 7.5 μL of triethylamine (54 μmol) in 2 mL of DCM for 17 h afforded 52 mg of **16** as a black solid in 61% yield after column chromatography (SiO_2, DCM/Et_2O: 95/5 then 90/10). ^1H NMR ($CDCl_3$) δ 7.16 (s, 1H, H_a); 5.54 (d, 1/2 H, $H_{e'\text{-I}}$, $^3J_{H-H}$ = 6.4 Hz); 5.35 (d, 1/2 H, $H_{e'\text{-II}}$, $^3J_{H-H}$ = 7.6 Hz); 5.23 (s, 2H, C$\underline{H}_2$-Ferrocene); 4.71−4.55 (m, 1H, $H_{b'\text{-III}}$ and $H_{b'\text{-IV}}$); 4.53−4.40 (m, 4H, H_k, H_o); 4.36−4.05 (m, 9H, Ferrocene); 3.98−3.81 (m, 1 H, H_{v-V-VI}); 3.78 (s, 3H, $H_{d'}$); 3.65−3.46 (m, 1/2 H, $H_{a'1\text{-III}}$; t, 2H, H_υ, $^3J_{H-H}$ = 6.8 Hz); 3.42 (dd, 1/2 H, $H_{a'1\text{-IV}}$, $^3J_{H-H}$ = 5.4 Hz, $^2J_{H-H}$ = 13.8 Hz); 3.23−2.85 (m, 2 H, $H_{a'2-III-IV}$, $H_{w2-V-VI}$); 2.64 (broad s, 2H, H_c); 2.54−2.35 (m, 1H, $H_{w1-V-VI}$); 1.91−1.71 (m, 4H, H_j, H_p); 1,70−1,18 (m, 18H, H_d-H_i, H_q-H_s); 1.45 (s, 9H, $H_{h'}$) ppm. ^{13}C NMR ($CDCl_3$) δ 176.6, 176.4, 174.4, and 174.3 (C_υ, C_x, $C_{f'}$); 171.3 ($C_{c'}$); 163.65, 163.64 (C_l, C_n); 145.40, 145.36, 145.27, 145.2, 144.9, 144.70, 144.68, 144.63, 144.62, 143.90, 143.89, 143.1, 143.03, 143.01, 142.2, 141.9, 140.97, 140.96, 139.00, 138.97, and 138.94 (Csp^2 C_{60}); 81.4 ($C_{Ferrocene}$); 80.4 ($C_{g'}$); 71.7 (Csp^3 C_{60}); 69.2, 69.1, 68.9, and 68.8 ($C_{Ferrocene}$); 67.5, 67.2 (C_k, C_o); 52.9, 52.8 ($C_{b'-III-IV}$, $C_{d'}$); 52.5 (*Cm*); 50.0 ($\underline{C}H_2$ Ferrocene); 39.1, 39.0, 38.9, and 38.4 (C_υ, C_{v-V-VI}); 36.0, 35.7, 34.7, and 34.2 ($C_{a'-III-IV}$, C_{w-V-VI}); 29.7, 29.5, 29.3, 29.2, 28.6, 28.4, 27.5, 26.4, 26.0, and 25.5 (C_{d-j}, C_{p-s}); 28.3 ($C_{h'}$); 25.8 (C_c) ppm. HRMS (ESI+) *m*/*z* calcd for $C_{104}H_{61}N_5O_{10}SFe$: 1627.3488 [$M^{+\bullet}$], found 1627.3528.

Synthesis of Fullerodendrimers. *Synthesis of* ***11***. [Cys]; *dendri*-PAMAM-$(CO_2tBu)_8$ **6** (92 mg, 56 μmol) was dissolved in 5 mL of freshly distilled DCM, argon was then bubbled through for 15 min. To this oxygen free solution was added 7.8 mg of DTT (51 μmol, 0.89 equiv relative to the dendrimer). The reaction mixture was stirred at room temperature for 48 h under argon. DTT was completely consumed according to TLC, whereas a new spot corresponding to the mercapto-functionalized *dendri*-PAMAM-$(CO_2tBu)_4$ was revealed with Ellman's reagent ($CHCl_3$-MeOH-NH_4OH: 3−1−0.02). This solution was used directly without further purification and was added under argon to an oxygen free solution containing 65 mg of compound **1** (56 μmol) and 8 μL of Et_3N (57 μmol) in 5 mL of DCM. The resulting reaction mixture was allowed to stir at room temperature for 24 h under argon and concentrated to dryness. Purification of the residue by column chromatography (SiO_2, DCM/MeOH: 97/3) then by permeation gel chromatography (Bio-Beads SX1, eluent toluene) afforded 35 mg of **11** as a black solid in 30% yield. ^1H NMR ($CDCl_3$) δ 7.06 (broad s, 2H, $H_{f'}$); 4.50−4.44 (m, 4H, H_k, H_o); 3.80 (dd, 1H, H_v, $^3J_{H-H}$ = 3.6 Hz, $^3J_{H-H}$ = 9.0 Hz); 3.48 (t, 2H, H_υ, $^3J_{H-H}$ = 7.3 Hz); 3.30−3.25 (m, 4H, $H_{g'}$); 3.11 (dd, 1H, H_{w1}, $^2J_{H-H}$ = 18.7 Hz, $^3J_{H-H}$ = 9.1 Hz); 3.06−2.70 (m, 16H, $H_{a'}$-$H_{c'}$, $H_{i'}$); 2.55−2.51 (m, 4H, $H_{h'}$); 2.46 (dd, 1H, H_{w2}, $^2J_{H-H}$ = 18.8 Hz, $^3J_{H-H}$ = 3.6 Hz); 2.38−2.31 (m, 12H, $H_{d'}$, $H_{j'}$); 2.16 (td, 2H, H_ω, $^3J_{H-H}$ = 7.0 Hz, $^4J_{H-H}$ = 2.6 Hz); 1.93 (t, 1H, H_a, $^4J_{H-H}$ = 2.6 Hz); 1.86−1.77 (m, 4H, H_j, H_p); 1.64−1.21 (m, 18H, H_d-H_i, H_q-H_s ; 1.43, s, 36H, $H_{m'}$) ppm. ^{13}C NMR ($CDCl_3$) δ 176.8, 174.8 (C_υ, C_x); 172.2, 172.0 ($C_{k'}$, $C_{e'}$); 163.8 (C_l, C_n); 145.45, 145.42, 145.35, 145.26, 145.0, 144.8, 144.71, 144.70, 144.0, 143.2, 143.1, 142.3, 142.0, 141.0, and 139.1 (Csp^2 C_{60}); 84.9 (C_b); 80.7 ($C_{l'}$); 71.7 (Csp^3 C_{60}); 68.3 (C_a); 67.6, 67.3 (C_k, C_o); 52.7, 52.6, 49.5, and 49.4 ($C_{b'}$-$C_{c'}$, $C_{h'}$-$C_{i'}$); 52.5 (C_m); 39.1 (C_υ); 39.0 (C_t); 37.4 ($C_{g'}$); 36.2 (C_w); 33.8, 33.6 ($C_{d'}$, $C_{j'}$); 29.6 ($C_{a'}$); 29.3, 29.2, 28.8, 28.7, 28.6, 28.3 ($C_{m'}$), 27.6, 26.5, 26.1, and 25.6 (C_{d-j}, C_{p-s}) ; 18.5 (C_c) ppm. HRMS (ESI+) *m*/*z* calcd for $C_{124}H_{109}N_6O_{16}S$: 1969.7621 [M + H^+], found 1969.7660.

Synthesis of ***13***. As described for **11**, the reaction of [Cys]; *dendri*-PAMAM-$(CO_2tBu)_8$ **6** (87 mg, 53 μmol) with 7 mg of DTT (45 μmol, 0.85 equiv relative to the dendrimer) in 5 mL of DCM for 48 h afforded a solution of the mercapto-functionalized *dendri*-PAMAM-$(CO_2tBu)_4$. This solution was added to a solution containing 58 mg of compound **7** (36 μmol) and 6 μL of Et_3N (43 μmol) in 2 mL of DCM. The resulting reaction mixture was allowed to stir at room temperature for 15 h and gave 33 mg of **13** as a black-red solid in 38% yield after purification by column chromatography (SiO_2, DCM/MeOH: 95/5) then by permeation gel chromatography (Bio-Beads SX1, eluent toluene). ^1H NMR ($CDCl_3$) δ 7.48 (s, 1H, H_a); 7.17 (d, 2H, H_5 or H_6, $^3J_{H-H}$ = 8.4 Hz); 7.07 (br s, 2H, $H_{f'}$); 6.96 (d, 2H, H_5 or H_6, $^3J_{H-H}$ = 8.4 Hz); 4.76 (t, 2H, H_8, $^3J_{H-H}$ = 4.8 Hz); 4.50−4.46 (m, 4H, H_k, H_o); 4.41 (t, 2H, H_7, $^3J_{H-H}$ = 4.9 Hz); 3.82 (dd, 1H, H_v, $^3J_{H-H}$ = 2.7 Hz, $^3J_{H-H}$ = 8.6 Hz); 3.49 (t, 2H, H_υ, $^3J_{H-H}$ = 7.2 Hz); 3.33−3.25 (m, 4H, $H_{g'}$); 3.11 (dd, 1H, H_{W1}, $^2J_{H-H}$ = 18.9 Hz, $^3J_{H-H}$ = 9.2 Hz); 3.05−2.69 (m, 16H, $H_{a'}$-$H_{c'}$, $H_{i'}$ and H_c); 2.60−2.46 (m, 4H, $H_{h'}$); 2.51 (s, 6H, H_4 or H_1); 2.44−2.25 (m, 17H, H_{w2}, $H_{d'}$, $H_{j'}$ and H_3); 1.90−1.75 (m, 4H, H_j, H_p); 1.74−1.25 (m, 24H, H_d-H_i, H_q-H_s, H_4 or H_1); 1.43 (s, 36H, $H_{m'}$); 0.97 (t, 6H, H_2, $^3J_{H-H}$ = 7.4 Hz). ^{13}C NMR ($CDCl_3$) δ 176.8, 174.9 (C_υ, C_x); 172.1,

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172.0 ($C_{e'}$, $C_{k'}$); 163.78, 163.77 (C_l, C_n); 158.4, 153.8 (Csp^2 Bodipy); 146.9 (C_b); 145.52, 145.45, 145.38, 145.36, 145.29, 145.0, 144.80, 144.79, 144.73, 144.71, 144.00, 143.97, 143.21, 143.19, 143.12, 143.08, 142.31, 142.30, 142.0, 141.08, and 141.05 (Csp^2 C_{60}); 139.8 (Csp^2 Bodipy); 139.1, 139.0 (Csp^2 C_{60}); 138.4, 132.9, 131.2, 129.8 (C_5 or C_6) and 129.0 (Csp^2 Bodipy); 122.0 (C_a); 115.1 (C_5 or C_6); 80.7 ($C_{l'}$); 71.8 (Csp^3 C_{60}); 67.6, 67.3 (C_k, C_o); 66.9 (C_7); 52.7, 52.6, 52.5 (C_m), 49.7, 49.5, and 49.4 (C_8, $C_{c'}$, $C_{c''}$, $C_{h'}$ and $C_{i'}$); 39.1, 39.0 (C_u, C_v); 37.4 ($C_{g'}$); 36.2 (C_w); 33.8, 33.6 ($C_{d'}$, $C_{j'}$); 29.8, 29.6, 29.5, 29.4, 29.3, 28.7, 28.5, 28.3 ($C_{m'}$), 27.6, 26.5, 26.1, 25.8, and 25.6 ($C_{a'}$, $C_{b'}$, $C_{d\text{-}j}$ and $C_{p\text{-}s}$); 17.2 (C_3), 14.8 (C_2), 12.6 and 12.0 (C_1, C_4) ppm. ^{19}F NMR ($CDCl_3$) δ −145.7 (q, 2F, $^1J_{F-B}$ = 32 Hz) ppm. ^{11}B NMR ($CDCl_3$) δ 1.96 (t, 1B, $^1J_{B-F}$ = 34 Hz) ppm. HRMS (ESI+) m/z calcd for $C_{149}H_{139}N_{11}O_{17}SBF_2$: 2434.0169 [M + H$^+$], found 2434.0190.

Synthesis of ***15***. [Cys]; *dendri*-PAMAM-$(CO_2tBu)_8$ **6** (134 mg, 82 μmol) was dissolved in 15 mL of freshly distilled DCM, argon was then bubbled through for 15 min. To this oxygen free solution was added 0.5 mL of a solution of DTT in DCM ([DTT] = 140 mmol/L, 0.85 equiv relative to the Dendron). The reaction mixture was stirred at room temperature for 48 h under argon. DTT was completely consumed according to TLC ($CHCl_3$-MeOH-NH_4OH: 3−1−0.02), whereas a new spot corresponding to the mercapto-functionalized *dendri*-PAMAM-$(CO_2tBu)_4$ was revealed with Ellman's reagent. This solution was used directly without further purification. To this solution was added an oxygen free solution containing 115 mg of compound **8** (82 μmol) and 11 μL of Et_3N (82 μmol) in 6 mL of DCM. The resulting reaction mixture was allowed to stir at room temperature for 24 h under argon and concentrated to dryness. Purification of the residue by column chromatography (SiO_2, DCM/MeOH: 94/6, next 92/8), then by permeation gel chromatography (Bio-Beads SX1, eluent toluene) afforded 57 mg of **15** as a black solid in 31% yield. ^1H NMR ($CDCl_3$) δ 8.26−7.90 (m, 9H, −C$\underline{H}_{ar}$ Pyrene); 7.12 (broad s, 2H, $H_{f'}$); 7.01 (s, 1H, H_a); 6.19 (s, 2H, −CH_2−Pyrene); 4.43 (t, 4H, H_k, H_o, $^3J_{H-H}$ = 6.5 Hz); 3.80 (dd, 1H, H_v, $^3J_{H-H}$ = 3.1 Hz, $^3J_{H-H}$ = 8.6 Hz); 3.46 (t, 2H, H_u, $^3J_{H-H}$ = 7.2 Hz); 3.28−3.30 (m, 4H, $H_{g'}$); 3.11 (dd, 1H, H_{w1}, $^2J_{H-H}$ = 18.9 Hz, $^3J_{H-H}$ = 9.1 Hz); 3.02 (t, 2H, $H_{a'}$, $^3J_{H-H}$ = 6.3 Hz); 2.86−2.72 (m, 14H, $H_{b'}$-$H_{c'}$, $H_{i'}$); 2.53 (m, 6H, $H_{h'}$, H_c); 2.45 (dd, 1H, H_{w2}, $^2J_{H-H}$ = 18.9, $^3J_{H-H}$ = 3.3 Hz); 2.27−2.40 (m, 12H, $H_{d'}$, $H_{j'}$); 1.82−1.70 (m, 4H, H_j, H_p); 1.60−1.11 (m, 18H, H_d-H_i, H_q-H_s); 1.43 (s, 36H, $H_{m'}$) ppm. ^{13}C NMR ($CDCl_3$) δ 176.8, 174.8 (C_u, C_x); 172.0 ($C_{k'}$, $C_{e'}$); 163.72, 163.69 (C_l, C_n); 148.8 (C_b); 145.4, 145.3, 145.24, 145.21, 145.17, 145.1, 144.8, 144.65, 144.62, 144.59, 143.9, 143.8, 143.0, 142.9, 142.2, 142.1, 141.9, 141.0, 140.9, 139.1, and 138.9 (Csp^2 C_{60}); 132.1, 131.3, 130.7, and 129.4 (C_{ar}); 129.1 128.4, 127.7, and 127.4 (CH_{ar}); 127.3 (C_{ar}); 126.5, 126.0, 125.9 (CH_{ar}); 125.2 (C_{ar}); 125.0 (CH_{ar}); 124.6 (C_{ar}); 122.2 (CH_{ar}); 120.6 (Ca); 80.70 ($C_{l'}$); 71.68 (Csp^3 C_{60}); 67.5, 67.3 (C_k, C_o); 52.7, 52.55, 49.5, and 49.3 ($C_{b'}$-$C_{c'}$, $C_{h'}$-$C_{i'}$); 52.45 (C_m); 52.36 ($\underline{C}H_2$ Pyrene); 39.1 (C_v); 38.9 (C_t); 37.3 ($C_{g'}$); 36.2 (C_w); 33.6, 33.5 ($C_{d'}$, $C_{j'}$); 29.8 ($C_{a'}$); 29.5, 29.4, 29.3, 29.2, 29.1, 28.6, 28.5, 27.5, 26.4, 26.0, and 25.8 ($C_{d\text{-}j}$, $C_{p\text{-}s}$); 28.2 ($C_{m'}$) and 25.5 (C_c) ppm. HRMS (ESI+) m/z calcd for $C_{141}H_{120}N_9O_{16}S$: 2226.8574 [M + H$^+$], found 2226.8596.

Synthesis of ***17***. As described for **15**, the reaction of [Cys]; *dendri*-PAMAM-$(CO_2tBu)_8$ **6** (133 mg in 15 mL of DCM, 81 μmol) with DTT ([DTT] = 137 mmol/L, 0.5 mL in DCM) for 48 h afforded a solution of the mercapto-functionalized *dendri*-PAMAM-$(CO_2tBu)_4$. To this solution was added a solution containing 113 mg of compound **9** (81 μmol) and 11 μL of Et_3N (81 μmol) in 5 mL of DCM. The resulting reaction mixture was allowed to stir at room temperature for 24 h and gave 60 mg of **17** as a black solid in 34% yield after purification by column chromatography (SiO_2, DCM/MeOH: 100/4), then by permeation gel chromatography (Bio-Beads SX1, eluent toluene). ^1H NMR ($CDCl_3$) δ 7.15 (s, 1H, H_a); 7.09 (broad s, 2H, H_F); 5.23 (s, 2H, $C\underline{H}_2$-Ferrocene); 4.465 (t, 2H, H_k or H_o, $^3J_{H-H}$ = 6.3 Hz) ; 4.455 (t, 2H, H_k or H_o, $^3J_{H-H}$ = 6.3 Hz); 4.25−4.15 (m, 9H, Ferrocene); 3.81 (dd, 1H, H_v, $^3J_{H-H}$ = 3.4 Hz, $^3J_{H-H}$ = 9.0 Hz); 3.48 (t, 2H, H_u $^3J_{H-H}$ = 7.3 Hz); 3.31−3.26 (m, 4H, $H_{g'}$); 3.11 (dd, 1H, H_{w1}, $^2J_{H-H}$ = 18.7 Hz, $^3J_{H-H}$ = 9.1 Hz); 3.02 (m, 2H, $H_{a'}$); 2.86−2.71 (m, 14H, $H_{b'}$-$H_{c'}$, $H_{i'}$); 2.63 (t, 2H, Hc, $^3J_{H-H}$ = 7.8 Hz); 2.58−2.50 (m, 4H, $H_{h'}$); 2.46 (dd, 1H, H_{w2}, $^2J_{H-H}$ = 18.7, $^3J_{H-H}$ = 3.7 Hz); 2.39−2.32 (m, 12H, $H_{d'}$, $H_{j'}$); 1.86−1.75 (m, 4H, H_j, H_p); 1.64−1.21 (m, 18H, H_d-H_i, H_q-H_s,) and 1.43 (s, 36H, $H_{m'}$) ppm. ^{13}C NMR ($CDCl_3$) δ 176.8, 174.8 (C_u, C_x); 172.1, 172.0 ($C_{k'}$, $C_{e'}$); 163.7 (C_l, C_n); 148.4 (C_b); 145.5, 145.4, 145.34, 145.26, 145.0, 144.8, 144.73, 144.70, 144.68, 143.98, 143.96, 143.17, 143.16, 143.09, 143.06, 142.3, 142.0, 141.04, 141.03, 139.1, 1389.0 (Csp^2 C_{60}); 120.0 (Ca); 81.3 ($C_{Ferrocene}$); 80.7 ($C_{l'}$); 71.7 (Csp^3 C_{60}); 69.1, 69.0 ($C_{Ferrocene}$); 67.6, 67.3 (C_k, C_o); 52.7, 52.6, 49.5, 49.4 ($C_{b'}$-$C_{c'}$, $C_{h'}$-$C_{i'}$); 52.5 (C_m); 49.9 ($\underline{C}H_2$ Ferrocene); 39.1 (C_v); 38.9 (C_t); 37.3 ($C_{g'}$); 36.2 (C_w); 33.7, 33.5 ($C_{d'}$, $C_{j'}$); 29.6 ($C_{a'}$); 29.4, 29.2, 28.7, 28.5, 27.6, 26.5, 26.1, and 25.6 ($C_{d\text{-}j}$, $C_{p\text{-}s}$); 28.2 ($C_{m'}$) and 25.8 (C_c) ppm. HRMS (ESI+) m/z calcd for $C_{135}H_{120}N_9O_{16}SFe$: 2210.7923 [M + H]$^+$, found 2210.7957.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01277.

^1H, ^{13}C and 2D NMR spectra of products **6**−**17**. Structures of fullerene reference compounds (**C_{60}-Bn** and **Full_ref**) along with the structure and numbering of compounds **6**−**17** used for ^1H and ^{13}C NMR signals. (PDF)

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Notes

The authors declare no competing financial interest.

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