Synthesis and Properties of Bingel-type Methanofullerene−π-Extended-TTF Diads and Triads

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Novel C_{60}/π-extended tetrathiafulvalene (exTTF) diads (**12a−c**) and triads [D_2A (**14a−c**) and DA_2 (**25**, **27a−c**)] have been synthesized by the Bingel cyclopropanation reaction of the respective exTTF-containing malonates and [60]fullerene. The reaction of exTTF-bismalonates with C_{60} affords the respective C_{60}−exTTF diads (**26a−c**) together with the triad C_{60}−exTTF−C_{60} (**25**, **27a−c**) and a regioisomeric mixture of bisadducts (**28b−c**). Theoretical calculations (PM3) predict the favored geometry for triads **14a−c** depending upon the orientation (up and down) of the 1,3-dithiole rings in the exTTFs, as well as the more stable regioisomers for the bisadducts **28**. Cyclic voltammetry measurements reveal that C_{60} and exTTF units do not interact in the ground state. Compounds **26a−c** and **27a−c** are not electrochemically stable. A photoinduced electron transfer leading to the formation of the radical pair ($C_{60}{}^{-}$−exTTF$^{•+}$) has been observed for compounds **14a−c**.

Introduction

The prominent features of fullerenes as electron acceptors and their versatility—especially in the excited states—led to the development of a wide variety of electroactive C_{60}-based donor−acceptor systems, especially light-induced charge-separation in artificial photosynthetic systems and photovoltaic devices.[1]

Among the different electron donor molecules covalently attached to [60]fullerene, tetrathiafulvalene (TTF),[2] and particularly π-extended tetrathiafulvalene (exTTF)[3] have been successfully used in the preparation of C_{60}-based diads that, upon radiation, form long-lived charge-separated states. The interesting photophysical behavior of C_{60}−TTF and C_{60}−exTTF diads has been

attributed to the small reorganization energy of C_{60} in electron-transfer reactions as well as to the gain of aromaticity undergone by the TTF and exTTF moieties upon oxidation. Both factors are believed to be responsible for the generation of stable radical pairs that show lifetimes in the range of nanoseconds for C_{60}−TTF **2** and several hundred of nanoseconds for the analogous C_{60}−exTTFs diads.[3]

On account of the outstanding lifetimes measured in C_{60}−exTTF diads, we have pursued the design of C_{60}−exTTF ensembles, in which the donor unit (exTTF) was covalently attached to the C_{60} core via cycloaddition reactions. To this end, fulleropyrrolidines (**1a−c**, **2a−c**)[3a] prepared by 1,3-dipolar cycloaddition reaction of "in situ" generated azomethyne ylides to C_{60},[4] Diels−Alder cycloadducts **3a−c** obtained by cycloaddition of "in situ" generated heterocyclic *o*-quinodimethanes to C_{60},[3b] and cycloaddition of "in situ" generated diazo compounds to C_{60} to form methanofullerenes **4a−c** by nitrogen extrusion[3c] have been recently reported. In all these systems (**1−4**), the synthetic approaches afforded the corresponding C_{60}−exTTF diads with a 1:1 donor:acceptor stoichiometry (Chart 1).

With the objective to achieve C_{60}−exTTF ensembles with D:A stoichiometries other than 1:1 (i.e., 2:1 and 1:2), we wish to report in this paper the synthesis of different diads and triads via employing the highly versatile Bingel reaction.[5] This cyclopropanation reaction of C_{60} leads efficiently to methanofullerenes. The reaction proceeds by addition of a stable α-halocarbanion to C_{60}, followed

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CHART 1

1a-c; n = 0
2a-c; n = 1

3a-c

a: R = H
b: R = SMe
c: R = S(CH$_2$)$_2$

4a-c
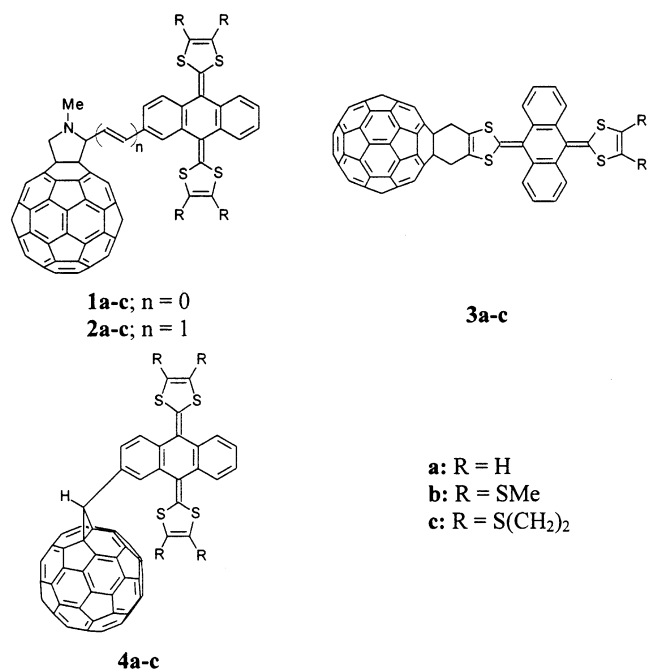
by an intramolecular nucleophilic substitution of the halide by the carbanion generated on the C$_{60}$ surface. It has also been shown that the cyclopropanation reaction can take place directly from malonates in the presence of I$_2$[6] or CBr$_4$[7] and even a base.

An important asset of the cyclopropanation reaction is that upon electrochemical reduction the removal of the cyclopropane ring adduct results in the formation of the parent C$_{60}$.[8] Addend removal via electrolytic reduction is, however, not only limited to Bingel-type adducts but also occurs for non-Bingel methanofullerenes.[9]

Therefore, we have carried out the synthesis of novel C$_{60}$–exTTF (**12a–c**, **26a–c**, **28a–c**) diads as well as C$_{60}$–(exTTF)$_2$ (**14a–c**) and (C$_{60}$)$_2$–exTTF (**25**, **27a–c**) triads by using the cyclopropanation Bingel reaction of suitably functionalyzed malonates and [60]fullerene. The redox properties of the new compounds were determined by cyclic voltammetry at room temperature, and semiempirical (PM3) theoretical calculations were performed to gain a better understanding of the geometric and electronic properties of the prepared systems.

Finally, photophysical measurements (fluorescence and transient absorption spectra) have been carried out to complement the present study.

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Results and Discussion

Synthesis of Diads and Triads (exTTF–C$_{60}$–exTTF). Diads C$_{60}$–exTTF (**12a–c**) were prepared in a multistep synthetic procedure, starting with commercially available 2-hydroxymethyl-9,10-anthraquinone (**5**). An outline is depicted in Scheme 1. After protection of the hydroxy group in **5** with tertbutyldiphenylsilyl in DMF and in the presence of imidazole, compound **6** was obtained in 89% yield. Then, the introduction of the 1,3-dithiole rings in **6** was carried out by the Wittig–Horner olefination reaction with the corresponding phosphonates (**7a–c**), which were, in turn, prepared by following the method previously reported.[10] Protected exTTFs (**8a–c**) were obtained in good yields (85–95%) by using an excess of phosphonate (1:4), favoring the formation of the biscondensed compounds **8a–c**. Further treatment of **8a–c** with tetrabutylammonium fluoride in THF at room temperature afforded the 2-hydroxymethyl-substituted exTTFs (**9a–c**) in very good yields (90–97%).

Compounds **9a–c** are interesting electron-donor building blocks, especially for the preparation of salts and charge-transfer complexes, since, in addition to their strong electron-donor character, they bear hydroxy groups. The latter form networks of hydrogen bonds with refined dimensionality in the solid state. The importance of hydrogen bonds in TTF derivatives to gain control over crystal architectures has been reviewed by Bryce.[11] Furthermore, exTTFs **9a–c** are suitably functionalized for chemical transformations.

Thus, we carried out the esterification reaction of **9a–c** with equimolar amounts of ethoxycarbonylacetic acid chloride in CH$_2$Cl$_2$ at 0 °C under argon atmosphere in the presence of pyridine. The corresponding compounds **10a–c** were formed in almost quantitative yields. Only compound **10c** was obtained in a lower yield (77%), as a consequence of the lower solubility of **9c** in the reaction medium. Compounds **10a–c**, similarly to their precursors, were obtained as yellow solids that were purified by column chromatography. All the compounds were characterized by analytical and spectroscopic methods (UV–vis, FTIR, ^{1}H and ^{13}C NMR, and MS) (see the Experimental Section).

Diads **12a–c** were prepared from **10a–c** by following two different procedures. The first route involves reaction of **10a** with CBr$_4$ and DBU in THF at −78 °C, which afforded the bromo derivative **11a** in moderate yields (40%). Further treatment of **11a** with sodium hydride in toluene, followed by processing with sulfuric acid, led to diad **12a** in a low yield (11%). Alternatively, diads **12a–c** were obtained with better yields (18–27%) and in shorter times (1.5–2h) by direct reaction of **10a–c** with C$_{60}$ and CBr$_4$/DBU in toluene. They were purified by column chromatography—first hexane to remove unreacted C$_{60}$ and then toluene/chloroform 1:1 to isolate **12a–c** as greenwish solids—and centrifugation with hexane, methanol, and diethyl ether.

Compounds **12a–c** have absorption maxima at 436–454 nm due to the presence of the exTTF moiety. The ^{13}C NMR spectra showed the presence of the fullerene sp^3 carbons at $\delta \sim 77.2$ and 71.2, thus confirming the

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SCHEME 1
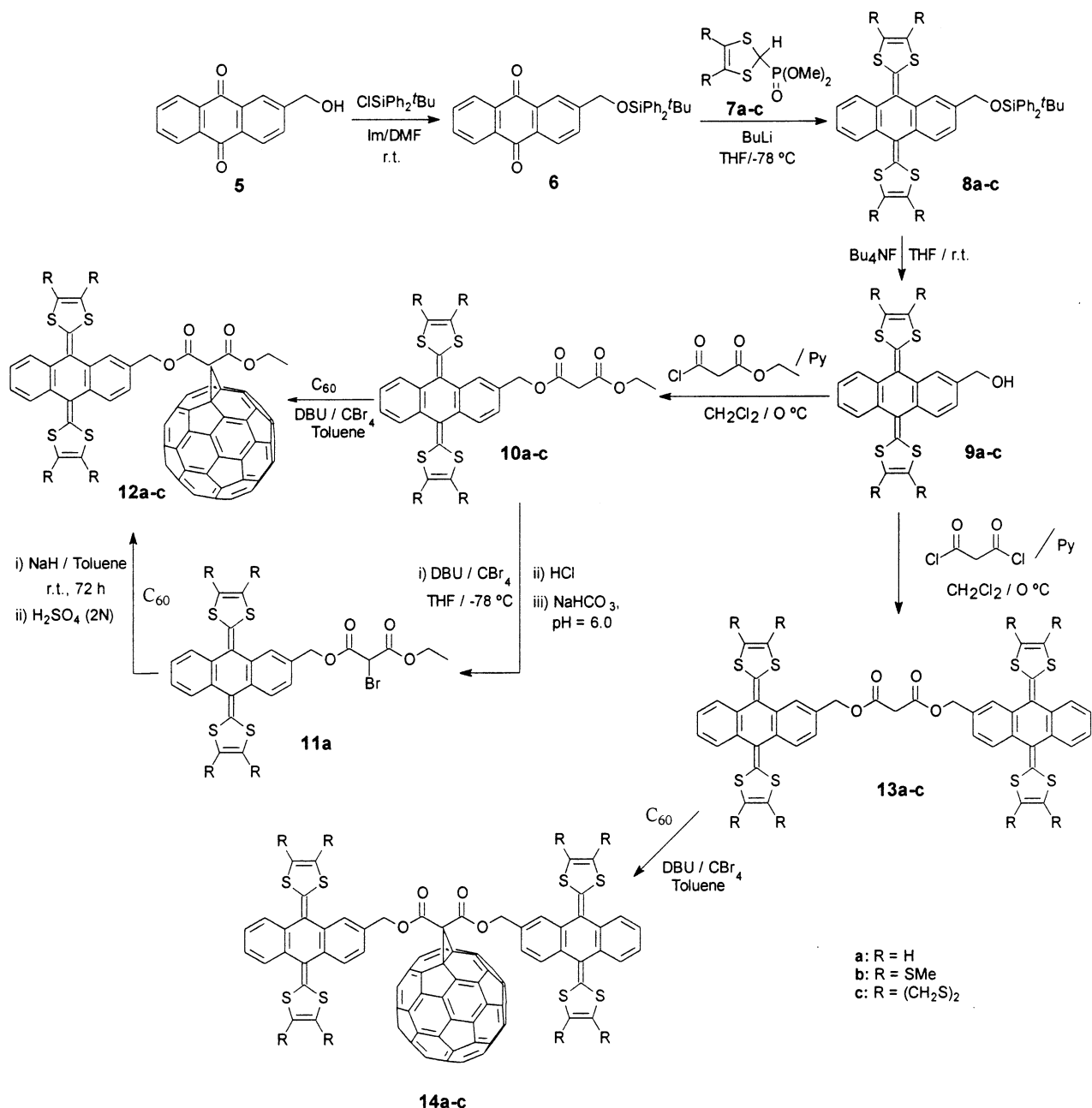
closed [6,6] nature of the fullerene unit. The MS (positive APCI) data (**12a**, m/z 1244; **12b**, m/z 1428; **12c**, m/z 1424) also confirmed the proposed structures.

Dimeric exTTF (**13a–c**) were prepared in 35–57% yields from **9a–c** by reaction with malonic acid dichloride in CH$_2$Cl$_2$ at 0 °C by using an excess of alcohol. These malonate derivatives, endowed with two exTTF units (**13a–c**), were reacted with C$_{60}$ and DBU/CBr$_4$ in toluene to form the respective Bingel adducts in moderate yields (16–25%, 60–70% yield based on the recovered C$_{60}$).

The structure of triads **14a–c** was determined on the basis of their spectroscopic data: UV–vis, FTIR, ^{1}H and ^{13}C NMR, and MS. Similar to what was found for diads **12a–c**, the ^{1}H NMR spectra of triads **14a–c** showed anisochronous protons for the –CH$_2$O– group. Thus, the –CH$_2$O– protons in **14a** appear as broad singlets at $\delta =$ 5.53, while they are only observed as an AB system ($J =$

11 Hz) for **14c** in which one of the doublets is not clearly observed due to the low solubility of this compound. Compound **14b**, which exhibited a good solubility, showed the –CH$_2$O– protons as two well-defined AB systems.

In addition, we carried out ^{1}H NMR studies at different temperatures in deuterated toluene to determine the coalescence temperature (20 °C) of these protons for the most soluble compound, **14b**. At room temperature the two doublets of the AB system coalescence into two singlets. Upon increasing the temperature to 29 °C, the other two doublets appear as two separate singlets. These low coalescence temperatures are responsible for the different behavior seen for the –CH$_2$O– protons in **14a–c**. On the other hand, the presence of the two –CH$_2$O– groups in **14a–c** as two different AB systems can be explained by the presence of different rotational isomers.
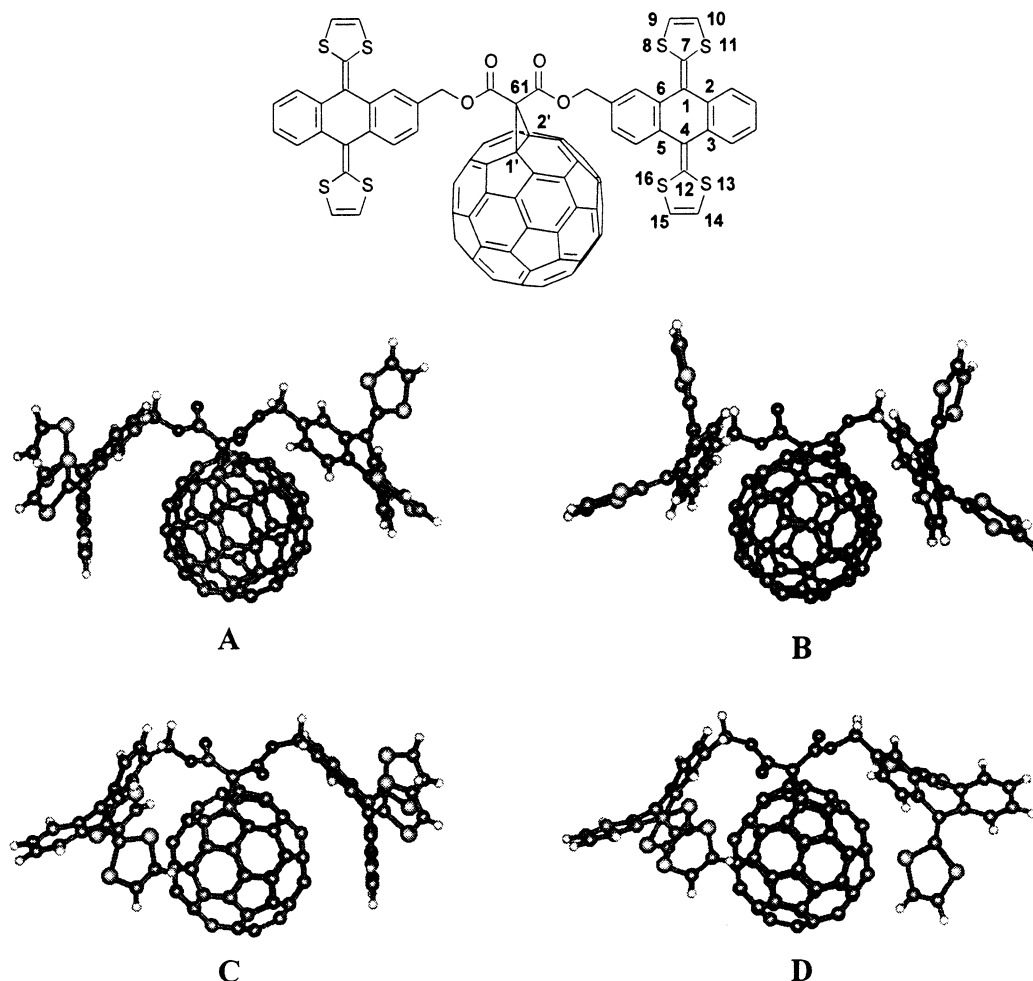
FIGURE 1. Different isomers (A−D) expected for **14a** depending on the relative orientation of the 1,3-dithiole rings (up or down). Calculations predict A as the favored isomer.

The latter effect is due to the flexibility of the spacer, connecting the exTTF and C_{60} units.

To determine the favored geometry of triads **14a–c** as well as to confirm the ^{1}H NMR observations, we carried out theoretical calculations with compound **14a** at the semiempirical PM3 (Hyperchem 5.0) level.

Depending on the relative orientation of the 1,3-dithiole rings in **14a**, namely, up or down, different isomers are expected (Figure 1). Our calculations predict A as the favored isomer. The latter is, however, only 0.28 kcal/mol more stable than the rotational isomer B. Larger enthalpy differences were found with isomers C (2.37 kcal/mol) and D (3.34 kcal/mol). Both isomers bear the 1,3-dithiole rings of one and two extended-TTF units, respectively, pointing to the C_{60} surface.

In summary, the small enthalpy difference between isomers, as well as the existence of rotational isomers due to the σ-bonds present in the connectivity of the exTTF unit to the C_{60} core account for the low coalescence temperatures seen in the ^{1}H NMR spectra.

Clearly, the theoretical calculations show the highly distorted geometry of the exTTF moiety. This is due to the strong steric interaction between the sulfur atoms of the 1,3-dithiole rings and the CH units in adjacent peri positions, forcing a butterfly-shaped structure. The distortion from planarity can be best described as a function

of the angle α, formed by the "wings of the butterfly" (dihedral angle C2−C1−C4−C5), and the angle γ, which defines the tilting of the 1,3-dithiole rings with respect to the C2−C3−C5−C6 plane (dihedral angle C7−C2−C6−C5). α and γ have values of 144.3° and 34.6°, respectively.

These values are in good agreement with X-ray data ($\gamma = 34.9°$)[12] for the parent exTTF unit and with earlier calculations.[13] Most importantly, the theoretical data indicate the lack of interaction between the donor (exTTF) and acceptor (C_{60}) units in the ground state, which agrees with the distance (6.63 Å) found between the sulfur atom and C_{60} in the most favored conformation A (Figure 1). This prediction also supports the UV−vis data, which did not show the presence of a low-energy charge-transfer band from the HOMO (−7.99 eV)—localized on the π-extended TTF donor moiety—to the LUMO (−2.80 eV) of the C_{60} acceptor unit.

Notably, the most significant changes are created on C_{60}, due to the presence of the fused cyclopopane ring. Thus, the bond length predicted between C1 and C2

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(1.548 Å) is 0.164 Å larger than that reported for the [6,6] bond in the parent C$_{60}$, and slighly shorter than that measured for the related bis(trimethylsilylbutadiinyl)-methanofullerene (1.574 Å)[14] and (3,4-dimethoxyphenyl)-methanofullerene (1.614 Å).[15]

Synthesis of Diads and Triads (C$_{60}$−exTTF−C$_{60}$). The preparation of C$_{60}$/exTTF ensembles with a different stoichiometry (C$_{60}$−exTTF−C$_{60}$) requires the use of bis-functionalized exTTFs. In this regard, bis-hydroxy functionalized exTTFs are readily available from anthraflavic acid (2,6-dihydroxy-9,10-anthraquinone, **15**), as outlined in Scheme 2.

The synthesis of the respective hydroxy-functionalized exTTFs (**21** and **22a**−**c**) requires protection of the hydroxy groups of anthraflavic acid (**15**) and 2,6-bis(2-hydroxyethyloxy)-9,10-anthraquinone (**17**), which was obtained from **15** by treatment with 2-bromoethanol under basic conditions. Further treatment of **15** and **17** with tertbutyldiphenylsilyl chloride afforded the hydroxy-protected compounds **16** and **18**, respectively, in good yields. Introduction of the 1,3-dithiole rings in quinones **16** and **18** was carried out by reaction with phosphonates **7a**−**c** in the presence of butyllithium at −78 °C, similarly to that reported above for compounds **8a**−**c**. It is worth mentioning that better yields (75−85%) were obtained when a quinone:phosphonate (1:6) stoichiometry was used.

Protecting groups were easily removed from **19** and **20a**−**c** by treatment with tetrabutylammonium fluoride in THF at room temperature, yielding the respective exTTF donors **21**[16] and **22a**−**c** as stable solids. The UV−vis spectra of these compounds showed an intense absorption band at around 430 nm.

The introduction of the malonate moiety, needed for the covalent linkage to the C$_{60}$ sphere, was carried out by reaction of **21** and **22a**−**c** with ethoxycarbonylacetyl chloride. Thus, compounds **23** and **24a**−**c**, endowed with two malonate moieties, respectively, were obtained in good yields (58−70%).

Compounds **23** and **24a**−**c**, as well as their precursors, were characterized by UV−vis, FTIR, ^{1}H and ^{13}C NMR, and MS. It is worth mentioning that, in addition to the expected aromatic and −CH$_2$O− signals, the active methylene groups of the malonate moieties were observed in all cases as singlets involving four protons at 3.65 ppm for **23** and ∼3.45 ppm for **24a**−**c** in the ^{1}H NMR spectra.

The synthesis of the C$_{60}$-based triads (C$_{60}$−exTTF−C$_{60}$) (**25** and **27a**−**c**) was carried out by reacting the respective bismalonates (**23** and **24a**−**c**) with C$_{60}$ (2:1 stoichiometry), using DBU and CBr$_4$ in *o*-DCB at 0 °C. Formation of bismethanofullerenes was observed even after short reaction times (i.e., 15−30 min). Attempts to carry out the reaction in toluene at room temperature, as reported in the literature for related systems,[17] led to a very fast reaction, including the formation of undesired byproducts. It was, however, impossible to isolate the intermediate monoadduct from the reaction mixture.

To favor the formation of triads, a 6-fold excess of C$_{60}$ was used in the reaction with malonates. Under these conditions, triad **25** was obtained from **23** in only 8% yield. The ^{1}H and ^{13}C NMR spectra showed a symmetric molecule with only a bridgehead carbon atom at ∼51−52 ppm, corresponding to the cyclopropane ring.

Reaction of **24a**−**c** with an excess (6:1) of C$_{60}$ afforded, similarly to **25**, triads **27a**−**c**, which were obtained in moderate yields (12−15%), together with other nonisolated compounds that were obtained in trace amounts.

A different result was obtained when a different stoichiometry of reagents (**24**:C$_{60}$, 1:1) was used, under the same reaction conditions (i.e., DBU, *o*-DCB, 0 °C). The outcome of the reaction, namely, the formation of three different organofullerenes (**26**−**28**), is summarized in Scheme 2.

The main reaction product diads **26a**−**c** were obtained in moderate yields (12−22%), together with a regioisomeric mixture of bis-addition products (**28a**−**c**) (6−8%). Isolation of the products, obtained from the reaction of **24a**−**c** with C$_{60}$, was carried out by column chromatography (silica gel). Unreacted C$_{60}$ was eluted with a toluene:ethyl acetate (50:1) mixture. Further purification was accomplished by centrifugation in hexane, methanol, and diethyl ether.

A second intramolecular Bingel reaction in **26a**−**c** brings about diads **28b**,**c**. In fact, TLC showed increasing yields of **28** simultaneously with decreasing yields in **26a**−**c**. Although observed by TLC, compound **28a** could not be isolated and, therefore, its precursor **26a** was obtained in much higher yield (22%) than the related analogues (**26b**,**c**; 12−13%).

Finally, despite the 1:1 stoichiometry used, triads **27a**−**c** were low-yield byproducts (∼1%), which were characterized by comparison with authentic samples.

It is worth mentioning that the different behavior of bis-malonates **23** and **24a**−**c** in the reaction with C$_{60}$ under Bingel conditions stems from the chain length connecting the malonate moieties and the central exTTF. Thus, the presence of two conformationally flexible −OCH$_2$CH$_2$O− groups in **26a**−**c** allows a subsequent intramolecular Bingel reaction, affording compounds **28b**,**c**.

Recently, tether-directed bis-cycloadducts forming cyclophane-type electroactive diads bearing porphyrins as donor moieties have been skillfully synthesized.[17] Photophysical studies carried out with some of these C$_{60}$−porphyrin donor−acceptor diads have disclosed one of the first experimental confirmations that back-electron-transfer from the one-electron-oxidized porphyrin to the radical anion of C$_{60}$ is placed deeply into the Marcus inverted region.[18] Similarly, an *o*-phenylenediamine has been also used as donor unit in this type of bis-cycloadduct.[19]

Compounds 28b,c were characterized on the basis of their spectroscopic data. The FTIR spectra showed, in

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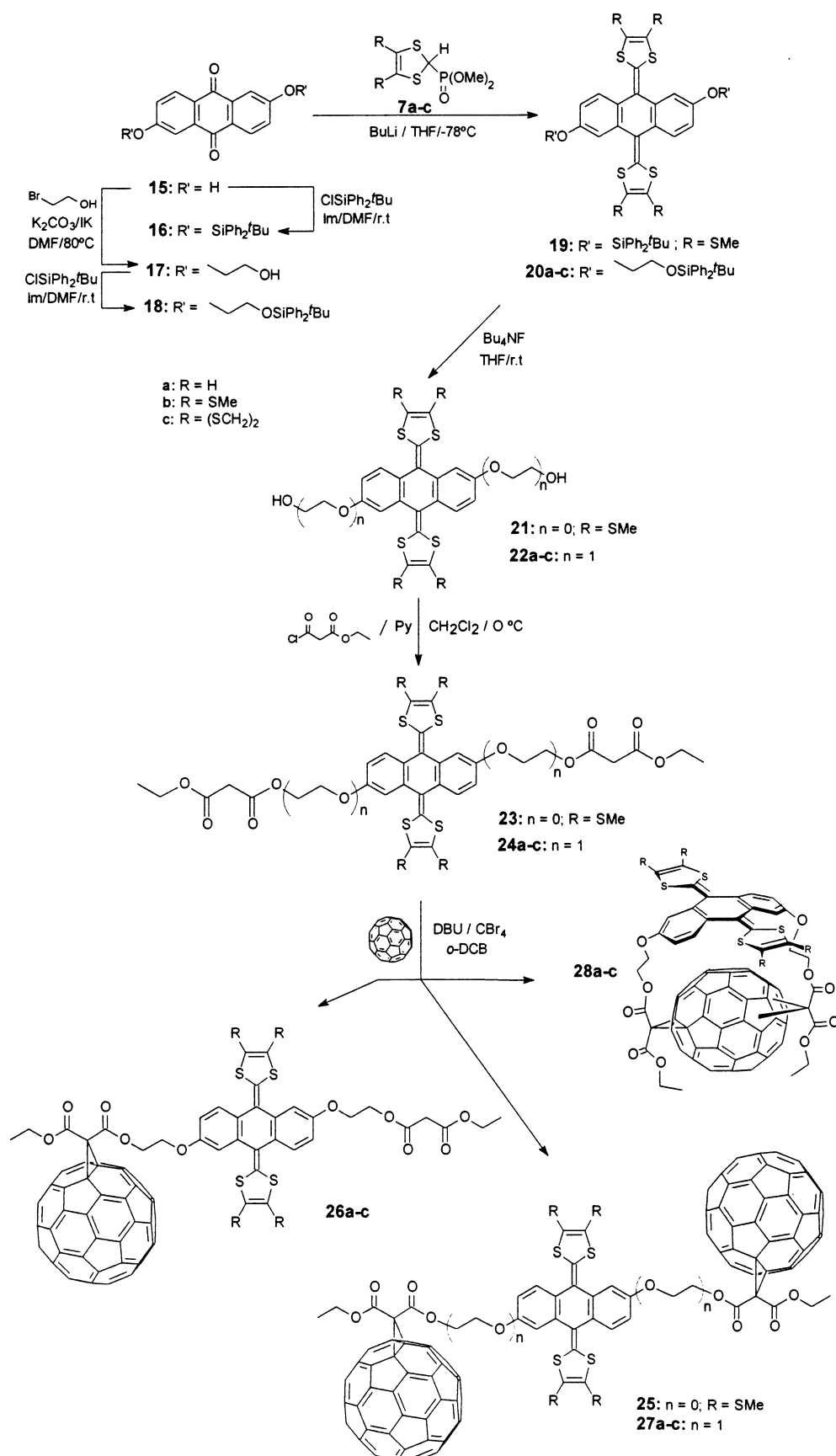(15) Osterodt, J.; Nieger, M.; Vögtle, F. *J. Chem. Soc. Chem. Commun.* **1994**, 1607.

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SCHEME 2

a: R = H
b: R = SMe
c: R = (SCH₂)₂

19: R' = SiPh₂ᵗBu ; R = SMe
20a-c: R' = OSiPh₂ᵗBu

21: n = 0; R = SMe
22a-c: n = 1

23: n = 0; R = SMe
24a-c: n = 1

28a-c

26a-c

25: n = 0; R = SMe
27a-c: n = 1

addition to the presence of the carbonyl groups, a low-intensity band at 526 cm⁻¹, thus confirming the bis-

addition pattern. Although the MS confirmed the proposed structures, the ¹H NMR spectra showed overlapping

multiplets, which suggests the presence of different isomers. The different possible regioisomers (*trans*-1, *trans*-2, *trans*-3, *e*) formed in compounds **28b**,**c** and the presence of two stereogenic bridgehead carbons in the two cyclopropane rings, as well as the possible (up and down) conformers resulting from the different orientation of the two 1,3-dithiole rings in the exTTF unit, can account for the observed complex ^{1}H NMR spectra.

Theoretical calculations at the semiempirical PM3 level (Hyperchem 5,0) were carried out on **28a** (R = H) in order to determine the minimum energy structure. According to the size and structure of the bis-malonate precursor (**24a**), formation of the *trans* regioisomers should occur preferentially.[20] In fact, among the different calculated structures (i.e., *trans*-4, *trans*-3, *trans*-2, *trans*-1, *e, cis*-3, *cis*-2, and *cis*-1), the *trans*-3 and *cis*-3 regioisomers had the most favored geometries, being around 0.5 kcal/mol more stable than the *e* isomer (Figure 2) and around 26 kcal/mol for the most unstable *cis*-1. For these regioisomers (*cis*-3, *trans*-3, and *e*), the exTTF moiety shows the 1,3-dithiole rings pointing away from the fullerene surface with a distance of 5−7 Å, which is too long for the existence of a through space intramolecular electron transfer in the ground state.

It is important to note that regioselectivity in bisaddition reactions may be governed by a kinetic control, as there are only small differences in the thermodynamic stability of the calculated regioisomers.

Triads (C$_{60}$−exTTF−C$_{60}$) were characterized by a variety of spectroscopic techniques, that is, UV−vis, FTIR, ^{1}H and ^{13}C NMR, and MS. The UV−Vis spectra showed intense transitions around 430 nm, stemming from the exTTF unit, which is responsible for the yellow color of compounds **27a**−**c** in toluene or *o*-DCB solutions. This intense band prevented the observation of the weak band at around 430 nm typical for 1,2-dihydrofullerenes.

In the ^{1}H NMR spectra of compounds **25** and **27a**−**c**, equivalent sets of protons—due to molecular symmetry— confirm the presence of two C$_{60}$ units. The ^{13}C NMR spectra, on the other hand, clearly showed the presence of the bridgehead carbon atom of the cyclopropane rings as a single signal at ∼51−52 ppm as well as the fullerene sp^3 carbon atoms at around 77 and 71 ppm (Figure 3). Furthermore, the structures were confirmed by mass spectroscopy. In addition to the molecular ions, as the most intense peaks, peaks were recorded that correspond to the loss of a fullerene unit (M$^+$ − C$_{60}$) for **27a**,**b**. Compound **25** presented the peaks corresponding to the loss of one (1542, M$^+$ − C$_{60}$) and two (822, M$^+$ − 2C$_{60}$) fullerene units.

Electrochemistry. The redox properties (Table 1) of the diads and triads have been studied by cyclic voltammetry (CV) at room temperature in toluene:acetonitrile (4:1) as solvent, along with those of C$_{60}$ and the parent π-extended 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (**29**).[12,21]

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trans-3

cis-3

e
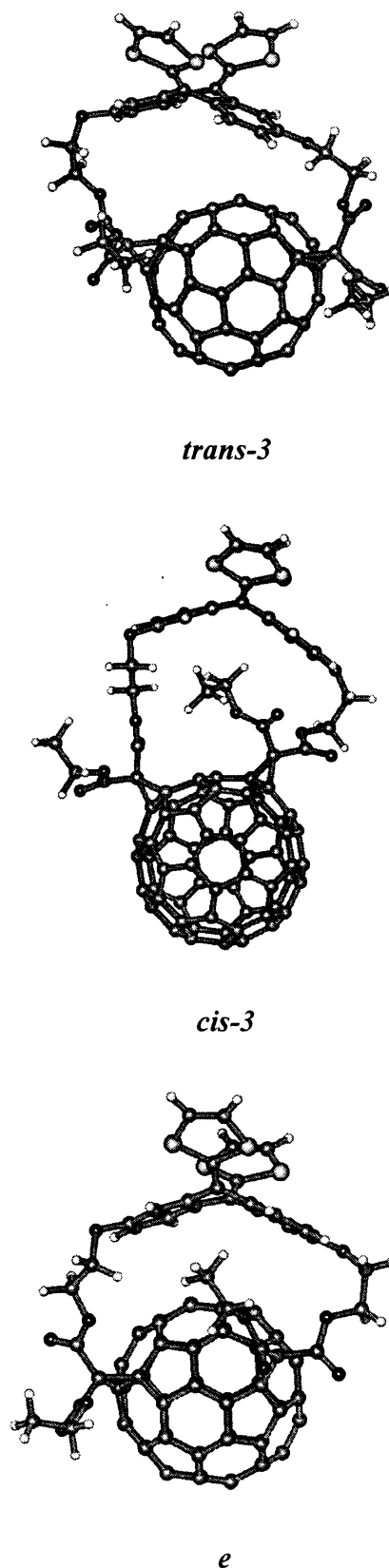
FIGURE 2. Theoretical calculations at the semiempirical PM3 level (Hyperchem 5,0) for **28a** predict the *trans*-3, *cis*-3, and *e* regioisomers as the most favored structures.

Clearly, the redox potential values show that substitution (mono- or bis-addition) on the C$_{60}$ surface modifies the electron-accepting properties of the C$_{60}$ unit. Thus,
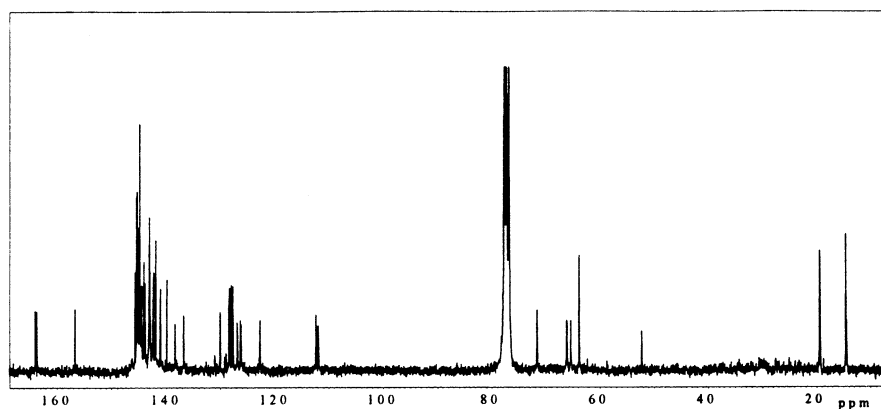
FIGURE 3. ^{13}C NMR spectrum of triad **27b**.

TABLE 1. Redox Potentials of the New Diads and Triads (V vs SCE)[a]

compd	E^1_{ox}	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}[b]
12a	0.50	−0.63	−0.99	−1.58	
12b	0.66	−0.65	−1.03	−1.55	−1.72
12c	0.67	−0.63	−1.02	−1.52	−1.70
14a	0.45	−0.62	−0.98	−1.50	
14b	0.67	−0.64	−1.04	−1.54	−1.69
14c	0.63	−0.67	−1.00	−1.53	−1.74
26b	0.55	−0.65	−1.08	−1.57	
		(−0.79)[c]	(−1.22)[c]	(−1.70)[c]	
27b	0.60	−0.67	−1.02	−1.52	
		(−0.75)[c]	(−1.24)[c]	(−1.66)[c]	
28b	0.55	−0.78	−1.23	−1.80	
C_{60}		−0.60	−1.07	−1.64	
29d	0.45				

[a] In toluene:MeCN (4:1); BuNClO$_4$ as supporting electrolyte; scan rate 200 mV/s. [b] Reduction of the organic addend. [c] Reduction peaks corresponding to the bis-cycloadduct **28b**. [d] In CH$_2$Cl$_2$.

three quasireversible reduction waves—corresponding to the first three reduction steps of the fullerene moiety—are observed in the voltammograms, similarly to that found for the parent C_{60} molecule. These reduction potentials appear, however, at slightly more negative values than those of C_{60}. This has been accounted for by the saturation of a double bond in the C_{60} framework, which raises the LUMO energy of the resulting modified fullerene.[22] In addition, another quasireversible reduction wave was observed at around −1.70 V in compounds **12b**,**c** and **14b**,**c**, which does not correspond to the fullerene core and, therefore, could be reasonably assigned to the reduction of the organic addend. In the remaining compounds **26**–**28**, this wave is apparently buried under the third reduction wave of the C_{60} core.

All compounds found in the oxidative scan showed a two-electron quasireversible oxidation wave to form the dication species of the exTTF moiety. As is shown in Table 1, substitution on the 1,3-dithiole rings with R = SMe, (SCH$_2$)$_2$ groups leads to an anodic shift of the oxidation potentials, which is in agreement with that observed for the parent molecule **29** and other related systems.[12,13,21] The two-electron nature as well as the

quasireversible behavior of the oxidation potential for π-extended TTF had been previously confirmed by Coulometric analysis[23] and other studies.[24] Only very recently, the π-radical cation of different quinonoid π-extended TTFs have been generated and characterized by means of time-resolved and steady-state radiation chemical techniques. These studies clearly revealed that the instability of the π-radical cation is governed by the disproportionation reaction of the π-radical cation into the corresponding dications.[25]

Triads **14a**−**c** bearing two exTTF units exhibit the same redox potential values as diads **12a**−**c** bearing only one exTTF unit, which indicates that both exTTF units in **14a**−**c** behave independently and, therefore, they present similar values as those of diads **12a**−**c**.

The electrochemical study of compounds derived from anthraflavic acid (**26**−**28**) was carried out on **26b**−**28b** (R = SMe), due to their better solubility in the solvent mixture. Surprisingly, the cyclic voltammogram of diad **26b** showed, in addition to the expected redox peaks at −0.65, −1.08, and −1.57 eV (see Table 1), the presence of additional reduction waves that clearly correspond to the reduction waves of the intramolecular bis-cycloadduct **28b**. Diads **28b** exhibits three reduction waves, significantly shifted to more negative values (−0.78, −1.23, −1.80 eV), which indicates the saturation of a second double bond of the C_{60} core, raising the LUMO energy even more.

The electrochemical formation of **28b** under the CV recording conditions of **26b** cannot be ruled out. Furthermore, the voltammogram of triad **27b** also showed, in addition to the expected oxidation and reduction waves (Table 1), the presence of other reduction waves corresponding to diad **28b**. Although formation of **28b** from **26b** is not straightforward, it has been clearly established for other related Bingel cycloadducts that a retro-cyclopropanation reaction (retro-Bingel reaction) under electrochemical[8] and chemical[26] reduction conditions can take

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TABLE 2. Photophysical Parameters of Diads 12a,c and Triads 14a−b

	12a		12c		14a		14b	
	$\Phi_{fluorescence}$	$\tau_{singlet}$, ps	$\Phi_{fluorescence}$	$\tau_{singlet}$, ps	$\Phi_{fluorescence}$	$\tau_{singlet}$, ps	$\Phi_{fluorescence}$	$\tau_{singlet}$, ps
toluene	0.7×10^{-4}	210	0.75×10^{-4}	230	0.7×10^{-4}	240	0.85×10^{-4}	280
benzonitrile	0.1×10^{-4}	55	0.15×10^{-4}	75	0.15×10^{-4}	60	0.25×10^{-4}	90

place. In this regard, we have recently proved the formation of bis-adducts from the corresponding monoadduct methanofullerenes by reductive electrolysis.[9c]

Related compounds **26a**,**c** and **27a**,**c**, although not collected in Table 1, exhibited similar behavior to that now reported for **26b** and **27b**. A better understanding of the electrochemical outcome of these compounds requires one to unravel the mechanism of the retro-Bingel reaction, which is currently under investigation by different research groups.[27]

Photophysics. To probe intramolecular electron-transfer events in methanofullerene-based C$_{60}$−exTTF diads and triads, fluorescence and transient absorption spectra of **12a−c** and **14a−c** were recorded in nonpolar toluene and also in polar benzonitrile solutions. For the fluorescence experiments we selected 330 nm as an excitation wavelength, where the exTTF moieties show a local minimum in their absorption spectra. Picosecond transient absorption measurements, on the other hand, were performed with 355-nm laser excitation.

In line with our previous observation, the fullerene fluorescence, which shows in a methanofullerene reference a quantum yield of 6.0×10^{-4}, is notably quenched (Table 2). In particular, quantum yields of 0.7×10^{-4} and 0.1×10^{-4} were measured in toluene and benzonitrile, respectively. Despite the strong fluorescence quenching, the features of the fluorescence spectra, with a room temperature *0−0 fluorescence maximum around 700 nm, remained unchanged relative to the methanofullerene reference. Interestingly, almost no difference is seen between the diad (**12a−c**) and the triad systems (**14a−c**). The solvent dependence speaks for a strongly exothermic electron transfer, evolving from the fullerene singlet excited state (1.76 eV) to form a meta-stable charge-separated radical pair, C$_{60}$$^{\bullet-}$−(exTTF)$^{\bullet+}$ (∼1.1 eV).

Complementary absorption measurements, following a 18-ps laser pulse, revealed the instantaneous formation of the fullerene singlet−singlet transition with a characteristic maximum around 900 nm. While in the methanofullerene reference a slow intersystem crossing (i.e., lifetime of around 1.8 ns) to the triplet manifold follows this initial photoexcitation, in **12a−c** and **14a−c** the singlet excited states decay appreciably faster. In toluene the lifetime ranges between 210 and 280 ps, and in benzonitrile it is as short as 50 ps. Differential absorption changes taken at the conclusion of these rapid decays allowed us to identify the product of these intramolecular processes. They show the fingerprint of the one-electron-oxidized form of exTTF, (exTTF)$^{\bullet+}$, with maxima typically at 660 nm (i.e., **12a** and **14a**) and 680 nm (i.e., **12b** and

14b). The reduced electron acceptor, C$_{60}$$^{\bullet-}$, shows its strongest absorption at 1040 nm.

Summary and Conclusions

In summary, we have carried out the synthesis of the first C$_{60}$/exTTF ensembles by using the Bingel cyclopropanation chemical approach with different donor (exTTF)/acceptor (C$_{60}$) stoichiometries (D−A, D−A−D, A−D−A). While substituted malonates bearing one or two exTTF donor units react with C$_{60}$ to afford the expected diads (**12a−c**) and triads (**14a−c**) without formation of other remarkable byproducts, the reaction of exTTF endowed with two malonate moieties yields different products. In particular, novel diads (**26a−c**) and triads (**25** and **27a−c**) were obtained together with the intramolecular bis-adducts (**28b,c**).

The electrochemical data reveal that both exTTF and C$_{60}$ electroactive moieties do not interact in the ground state. The CV studies of diad **26b** and triad **27b** showed the presence of bis-adducts **28b** in their voltammogram. Although formation of **28b** is not clear at present, formation under reductive electrochemical conditions is suggested.

Theoretical calculations at the semiempirical PM3 level predict the existence of different conformational isomers for triads **14** depending upon the orientation, that is, either up or down, of the 1,3-dithiole rings of the exTTF units, as well as for diads **28**, for which different regioisomers are energetically favored.

Photophysical studies clearly show the fingerprint of the radical cation exTTF$^{\bullet+}$, with maxima typically at around 660−680 nm, and the radical anion C$_{60}$$^{\bullet-}$, which shows its strongest absorption at 1040 nm, thus confirming the photoinduced electron transfer and the formation of the charge-separated state in the compounds studied.

Experimental Section

Cyclic voltammograms were recorded on a potentiostat/galvanostat, equipped with Model 250 software for electrochemical analysis by using a GCE as working electrode, SCE as reference electrode, Bu$_4$N$^+$ClO$_4$$^-$ (0.1 M), CH$_2$Cl$_2$ as solvent, and scan rate of 200 mV/s.

Synthesis of C$_{60}$−exTTF Diads (12a−c). To a solution of C$_{60}$ (72 mg, 0.10 mmol), CBr$_4$ (50 mg, 0.15 mmol), and the respective ethyl malonate derivative (**10a−c**) (0.15 mmol) in toluene at room temperature was added DBU (45μL, 0.30 mmol). The reaction was monitored by TLC, and after 2 h, formation of bisadducts was observed. The solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel, first with cyclohexane to elute the unreacted C$_{60}$, and then cyclohexane:toluene (1:1) as the eluent. Further purification was accomplished by three centrifugations using hexane, methanol, and ethyl ether as solvents.

61-[9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydro-2-anthracenylmethyloxycarbonyl]-61-(ethoxycarbonyl)-1,2-methano[60]fullerene (12a). 32% yield (85% based on unreacted C$_{60}$). FTIR (KBr): 2922, 2853, 1743 (C=O), 1637, 1545, 1511, 1450, 1425, 1265, 1230, 1174, 1094, 1057, 1019,

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800, 753, 703, 644, 580, 551, 526 (C_{60}) cm^{-1}. ^{1}H NMR (CDCl$_3$/CS$_2$ 1/1, 300 MHz), δ: 7.60–7.39 (7H, m, ArH), 6.31–6.28 (4H, m, CH=), 5.62 (1H, AB, J = 11.0 Hz, ArCH$_2$O), 5.54 (1H, AB, J = 11.0 Hz, ArCH$_2$O), 4.51 (2H, q, J = 7.1 Hz, OCH$_2$), 1.41 (3H, t, J = 7.1 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$, 75 MHz), δ: 163.02 (C=O), 162.92 (C=O), 144.33, 144.23, 144.02, 143.76, 143.74, 143.50, 143.00, 142.85, 142.07, 140.88, 139.96, 138.80, 137.60, 135.22, 134.89, 134.29, 131.44, 126.27, 125.44, 125.42, 125.18, 124.50, 124.40, 124.13, 116.58, 116.41, 116.33, 77.17 ($C_{sp^3}C_{60}$), 74.32 ($C_{sp^3}C_{60}$), 68.48 (CH$_2$O), 63.25 (CH$_2$O), 51.86 (C), 13.93 (CH$_3$). MS m/z (%): 1244 (M$^+$, 20). UV–vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 436 (sh, 4.37), 428 (4.37), 416 (sh, 4.34), 366 (4.37), 328 (4.63), 258 (5.12), 242 (5.10) nm.

61-[9,10-Bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-9,-10-dihydro-2-anthracenylmethyloxycarbonyl]-61-(ethoxycarbonyl)-1,2-methano[60]fullerene (12b). 27% yield (73% based on unreacted C$_{60}$). FTIR (KBr): 2968, 2925, 2919, 2916, 1745 (C=O), 1637, 1541, 1534, 1507, 1494, 1451, 1425, 1266, 1231, 1203, 1186, 1095, 1057, 1018, 753, 703, 669, 581, 552, 526 cm^{-1}. ^{1}H NMR (CDCl$_3$/CS$_2$ 1/1, 300 MHz), δ: 7.48–7.20 (7H, m, ArH), 5.66 (1H, AB, J = 11.5 Hz, ArCH$_2$O), 5.55 (1H, AB, J = 11.5 Hz, ArCH$_2$O), 4.53 (2H, q, J = 7.1 Hz, OCH$_2$), 2.40 (12H, s, SCH$_3$), 1.42 (3H, t, J = 7.1 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$/CS$_2$ 1/1, 75 MHz), δ: 163.10 (C=O), 163.06 (C=O), 145.04, 144.94, 144.90, 144.85, 144.67, 144.60, 144.44, 144.13, 144.03, 143.68, 143.58, 142.84, 142.77, 142.60, 142.01, 141.59, 141.46, 140.70, 140.66, 139.51, 138.05, 138.00, 135,10, 134,-82, 134,26, 134,23, 132,65, 132,37, 132,31, 130,64, 127,24, 126,-52, 126,44, 126,24, 126,18, 125,59, 125,55, 125,29, 123,04, 122,78, 77,21 ($C_{sp^3}C_{60}$), 71,24 ($C_{sp^3}C_{60}$), 68,35 (CH$_2$O), 63,34 (CH$_2$O), 51,70 (C), 19,16 (SCH$_3$), 19,12 (SCH$_3$), 19,07 (2SCH$_3$), 14,17 (CH$_3$). MS m/z (%): 1427 (M$^+$, 31), 720 (C$_{60}$, 10). UV–vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 442 (4.42), 428 (sh, 4.38), 362 (4.45), 328 (4.63), 258 (5.14), 246 (5.12) nm.

61-[9,10-Bis(1,3-dithiol-4,5-ethylenedithio-2-ylidene)-9,10-dihydro-2-anthracenylmethyloxycarbonyl]-61-(ethoxycarbonyl)-1,2-methano[60]fullerene (12c). 18% yield (63% based on unreacted C$_{60}$). FTIR (KBr): 2970, 1919, 1745 (C=O), 1639, 1541, 1507, 1451, 1424, 1384, 1365, 1284, 1266, 1252, 1231, 1203, 1186, 1175, 1110, 1095, 1058, 1017, 754, 704, 641, 581, 563, 552, 526 (C$_{60}$) cm^{-1}. ^{1}H NMR (CDCl$_3$/CS$_2$ 1/1, 300 MHz), δ: 7.51–7.27 (7H, m, ArH), 5.60 (1H, AB, J = 11.7 Hz, ArCH$_2$O), 5.53 (1H, AB, J = 11.7 Hz, ArCH$_2$O), 4.51 (2H, q, J = 7.1 Hz, OCH$_2$), 3.32–3.29 (8H, m, SCH$_2$), 1.43 (3H, t, J = 7.1 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$/CS$_2$ 1/1, 75 MHz), δ: 162.89 (C=O), 162.77 (C=O), 145.04, 145.02, 144.94, 144.85, 144.81, 144.67, 144.64, 144.55, 144.44, 144.41, 144.35, 144.20, 144.15, 143.61, 143.52, 142.88, 142.74, 142.68, 142.64, 142.52, 141.93, 141.50, 140.60, 139.42, 138.31, 138.05, 135.13, 134.90, 134.29, 132.51, 130.98, 128.75, 127.22, 126.40, 126.15, 125.57, 125.29, 125.23, 122.75, 122.45, 111.14, 110.90, 110.83, 77.21 ($C_{sp^3}C_{60}$), 71.25 ($C_{sp^3}C_{60}$), 68.27 (CH$_2$O), 63.22 (CH$_2$O), 46.85 (C), 29.73 (SCH$_2$), 14.19 (CH$_3$). MS m/z (%): 1424 (M$^+$, 11). UV–vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 454 (4.27), 428 (4.17), 328 (4.55), 258 (5.06), 242 (sh, 5.01) nm.

Synthesis of Di[9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydro-2-anthracenylmethyl] Malonates (13a–c). To a solution of compound **9a–c** (0.5 mmol) in dry CH$_2$Cl$_2$ (30 mL) at room temperature and under argon atmosphere was added dry pyridine (35 μL, 0.495 mmol) was added. The mixture was cooled in an ice bath. Malonic acid dichloride (24.5 mg, 0.245 mmol) in dry CH$_2$Cl$_2$ (1 mL) was added dropwise during 10 min. The mixture was stirred at 0 °C for 2 h, allowed to warm to 20 °C, and then let stand overnight. Water (75 mL) was added and the residue extracted with CH$_2$Cl$_2$ (3 × 100 mL). The combined extracts were dried (Na$_2$SO$_4$) and filtered out, and the solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel using hexane:dichloromethane mixtures as eluent.

Di[9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydro-2-anthracenylmethyl] Malonate (13a). 58% yield. Mp: 183–185 °C (dec). Anal. (Calcd) for C$_{45}$H$_{28}$S$_8$O$_4$: C, 61.43 (60.81); H, 3.86

(3.18); S, 27.81 (28.80). IR (KBr): 3060, 2960, 2920, 2850, 1750 (C=O), 1735 (C=O), 1550, 1510, 1450, 1425, 1375, 1330, 1290, 1260, 1150, 1000, 900, 890, 835, 810 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz), δ: 7.68–7.62 (7H, m, ArH), 7.29–7.21 (7H, m, ArH), 6.26–6.21 (8H, m, CH=), 5.23 (4H, s, CH$_2$O), 3.54 (2H, s, CH$_2$). ^{13}C NMR (CDCl$_3$, 75 MHz), δ: 166.14 (2C=O), 135.31, 135.12, 135.21, 135.10, 132.63, 132.61, 125.87, 125.85, 125.60, 125.10, 124.83, 124.77, 124.64, 124.58, 121.51, 121.50, 121.47, 117.15, 117.12, 117.10, 117.06, 117.02, 116.98, 116.96, 116.95, 67.04 (2CH$_2$O), 41.64 (CH$_2$). MS m/z (%): 888 (M$^+$, 86), 830 (M$^+$ − S(CH)$_2$, 18). UV–vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 432 (4.99), 412 (sh, 4.91), 366 (4.77), 274 (4.61), 240 (2.54) nm.

Di[9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-9,10-dihydro-2-anthracenylmethyl] Malonate (13b). 57% yield. Mp: 183–185 °C (dec). Anal. (Calcd) for C$_{53}$H$_{44}$S$_{16}$O$_4$: C, 50.92 (50.64); H, 3.78 (3.53). IR (KBr): 2960, 2930, 2860, 1760 (C=O), 1745 (C=O), 1535, 1500, 1450, 1425, 1320, 1280, 1140, 980, 930, 755 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz), δ: 7.53–7.26 (14H, m, ArH), 5.25 (4H, s, CH$_2$O), 3.53 (2H, s, CH$_2$), 2.40–2.37 (24H, s, SCH$_3$). ^{13}C NMR (CDCl$_3$, 75 MHz), δ: 166.09 (C=O), 135.01, 134.91, 134.66, 134.64, 134.44, 133.20, 131.69, 126.38, 126.07, 125.71, 125.63, 125.37, 125.12, 125.01, 123.10, 67.05 (2CH$_2$O), 41.66 (CH$_2$), 19.09 (8SCH$_3$). MS m/z (%): 1255 (M$^+$, 52). UV–vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 444 (5.12), 376 (4.88), 278 (5.02), 246 (5.35) nm.

Di[9,10-bis(1,3-dithiol-4,5-ethylenedithio-2-ylidene)-9,10-dihydro-2-anthracenylmethyl] Malonate (13c). 35% yield. Mp: 215–218 °C (dec). FTIR (KBr): 2922, 2850, 1734 (C=O), 1560, 1541, 1508, 1458, 1412, 1294, 1144, 1009, 754 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz), δ: 7.49–7.44 (8H, m, ArH), 7.31–7.24 (6H, m, ArH), 5.25 (4H, s, CH$_2$O), 3.54 (2H, s, CH$_2$), 3.28–3.26 (16H, m, SCH$_2$). ^{13}C NMR (CDCl$_3$, 50 MHz), δ: 166.0 (2C=O), 134.8, 134.4, 133.3, 130.0, 126.3, 125.6, 125.4, 125.3, 125.2, 111.0, 66.9 (2CH$_2$O), 41.5 (CH$_2$), 29.5 (8SCH$_2$). MS m/z (%): 1248 (M$^+$, 2). UV–vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 450 (4.70), 430 (sh, 4.59), 388 (4.38), 278 (4.61), 242 (4.96) nm.

Synthesis of (exTTF)$_2$–C60 Triads (14a–c). To a solution of C$_{60}$ (72 mg, 0.10 mmol), CBr$_4$ (50 mg, 0.15 mmol), and the respective malonate derivative (**13a–c**) (0.15 mmol) in toluene at room temperature was added DBU (45 μL, 0.30 mmol). The reaction was monitored by TLC. After 4–6 h formation of bis-adducts was observed and the reaction was stopped. The solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel, first with cyclohexane to elute the unreacted C$_{60}$ and then using cyclohexane:toluene (1:1) as the eluent. Further purification was accomplished by three centrifugations using hexane, methanol, and ethyl ether as solvents, respectively.

61-Bis[9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydro-2-anthracenylmethyloxycarbonyl]-1,2-methano[60]-fullerene (14a). 25% yield (60% based on unreacted C$_{60}$). FTIR (KBr): 2918, 2848, 1745 (C=O), 1541, 1507, 1457, 1428, 1229, 1182, 800, 756, 701, 669, 645, 577, 527 (C$_{60}$) cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz), δ: 7.87–7.27 (14H, m, ArH), 6.31–6.19 (8H, m, CH=), 5.53 (4H, s br, CH$_2$O). ^{13}C NMR (CDCl$_3$, 75 MHz), δ: 163.30 (C=O), 144.95, 144.94, 144.75, 144.70, 144.49, 144.31, 144.25, 143.65, 143.03, 142.78, 142.65, 142.06, 141.70, 141.69, 140.64, 138.84, 136.70, 136.69, 136.56, 136.55, 135.81, 135.63, 135.11, 135.00, 132.13, 126.68, 126.10, 126.01, 125.57, 125.02, 125.23, 124.89, 121.61, 121.37, 117.18, 77.20 ($C_{sp^3}C_{60}$), 71.32 ($C_{sp^3}C_{60}$), 68.79 (CH$_2$O), 68.75 (CH$_2$O), 47.21 (C). MS m/z (%): 1607 (M$^+$, 5), 720 (C$_{60}$, 24). UV–vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 436 (4.37), 418 (sh, 4.35), 368 (4.39), 328 (4.46), 256 (4.94), 234 (5.10) nm.

61-Bis[9,10-bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-9,10-dihydro-2-anthracenylmethyloxycarbonyl]-1,2-methano[60]fullerene (14b). 30% yield (70% based on unreacted C$_{60}$). FTIR (KBr): 2918, 2850, 1748 (C=O), 1705 (C=O), 1576, 1540, 1496, 1452, 1424, 1265, 1226, 1200, 1184, 1094, 1057, 966, 890, 824, 753, 669, 642, 578, 558, 526 (C$_{60}$) cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz), δ: 7.52–7.25 (14H, m, ArH),

5.65 (1H, AB, J = 12.2 Hz, CH$_2$O), 5.64 (1H, AB, J = 11.6 Hz, CH$_2$O), 5.54 (1H, AB, J = 11.6 Hz, CH$_2$O), 5.52 (1H, AB, J = 12.2 Hz, CH$_2$O), 2.40−2.39 (24H, m, SCH$_3$). ^{13}C NMR (CDCl$_3$, 75 MHz), δ: 167.75 (C=O), 163.34 (C=O), 145.02, 144.96, 144.89, 144.73, 144.61, 144.52, 144.25, 143.66, 143.05, 142.65, 142.06, 142.03, 141.65, 141.51, 140.66, 138.78, 138.71, 135.15, 135.00, 134.91, 134.36, 134.34, 132.69, 132.41, 131.99, 131.91, 130.89, 130.87, 128.82, 128.77, 127.03, 126.55, 126.40, 125.70, 125.66, 125.58, 125.36, 122.97, 122.71, 77.20 (C$_{sp^3}$C$_{60}$), 71.21 (C$_{sp^3}$C$_{60}$), 68.63 (CH$_2$O), 68.12 (CH$_2$O), 51.70 (C), 19.22 (SCH$_3$), 19.20 (SCH$_3$). MS *m/z* (%): 1976 (M$^+$, 31), 720 (C$_{60}$, 100). UV−vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 442 (4.56), 420 (sh, 4.48), 370 (4.50), 328 (4.57), 258 (5.09), 242 (5.13), 234 (5.15) nm.

61-Bis[9,10-bis(1,3-dithiol-4,5-ethylenedithio-2-ylidene)-9,10-dihydro-2-anthracenylmethyloxycarbonyl]-1,2-methano[60]fullerene (14c). 16% yield (65% based on unreacted C$_{60}$). FTIR (KBr): 2920, 1747 (C=O), 1635, 1540, 1506, 1455, 1423, 1284, 1226, 1201, 1058, 754, 668, 642, 526 (C$_{60}$) cm^{-1}. ^{1}H NMR (CDCl$_3$/CS$_2$ 1/1, 300 MHz), δ: 7.44−7.27 (14H, m, ArH), 5.63 (2H, AB, J = 11.0 Hz, CH$_2$O), 5.52−5.45 (2H, AB, J = 11.0 Hz, CH$_2$O), 3.31−3.28 (16H, m, SCH$_2$). MS *m/z* (%): 1967 (M$^+$, 59). UV−vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 452 (4.39), 428 (sh, 4.29), 326 (4.47), 256 (sh, 5.01), 234 (5.13) nm.

Synthesis of Bismalonates (23 and 24a−c). To a solution of the respective alcohol derivative (**21 or 22a−c**) (0.25 mmol) in dry CH$_2$Cl$_2$ (30 mL) at room temperature and under argon atmosphere was added dry pyridine (68 μL, 0.85 mmol). The mixture was cooled in an ice bath. Ethoxycarbonylacetic acid chloride (93 μL, 0.75 mmol) in dry CH$_2$Cl$_2$ (1 mL) was added dropwise during 10 min. The mixture was stirred at 0 °C for 2 h and then allowed to warm to 20 °C to stand overnight. Water (75 mL) was added and the residue extracted with CH$_2$Cl$_2$ (3 × 100 mL). The combined extracts were dried (Na$_2$SO$_4$) and filtered out, and the solvent was removed under reduced pressure. Purification of products was achieved by column chromatography on silica gel using hexane:dichloromethane mixtures as eluent.

9,10-Bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-2,6-bis-(1,5-dioxa-2,4-dioxoheptyl)-9,10-dihydroanthracene (23). 64% yield. Mp: 129−131 °C. FTIR (KBr): 2924, 2852, 2740, 1763 (C=O), 1738 (C=O), 1602, 1560, 1533, 1469, 1410, 1367, 1329, 1261, 1238, 1188, 1134, 1094, 1026, 966, 891 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz), δ: 7.54 (2H, d, $J_{3,4}$ = 8.4 Hz, ArH$_4$), 7.31 (2H, d, $J_{1,3}$ = 2.2 Hz, ArH$_1$), 7.07 (2H, dd, $J_{3,4}$ = 8.4 Hz, $J_{1,3}$ = 2.2 Hz, ArH$_3$), 4.29 (4H, q, J = 7.3 Hz, OCH$_2$), 3.65 (4H, s, CH$_2$), 2.40 (12H, s, SCH$_3$), 1.35 (6H, t, J = 7.3 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$, 50 MHz), δ: 166.03 (2C=O), 164.91 (2C=O), 148.36 (2C$_2$), 136.01, 132.82, 132.45, 126.28, 125.90, 121.75, 118.97, 118.29, 61.85 (2OCH$_2$), 41.72 (CH$_2$), 19.10 (2SCH$_3$), 19.06 (2SCH$_3$), 14.14 (2CH$_3$). MS *m/z* (%): 847 (M$^+$ + Na, 100). UV−vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 242 (4.23), 268 (sh, 3.88), 373 (3.74), 440 (3.98) nm.

9,10-Bis(1,3-dithiol-2-ylidene)-2,6-bis(1,4,8-trioxa-5,7-dioxodecyl)-9,10-dihydroanthracene (24a). 62% yield. Mp: 62−65 °C. FTIR (KBr): 2767, 1734 (C=O), 1603, 1545, 1508, 1458, 1412, 1369, 1026, 966, 798, 756 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz), δ: 7.59 (2H, d, $J_{3,4}$ = 8.5 Hz, ArH$_4$), 7.22 (2H, d, $J_{1,3}$ = 2.4 Hz, ArH$_1$), 6.82 (2H, dd, $J_{3,4}$ = 8.5 Hz, $J_{1,3}$ = 2.4 Hz, ArH$_3$), 6.29 (4H, s, CH=), 4.54 (4H, t, J = 4.2 Hz, ArOCH$_2$), 4.25 (4H, t, J = 4.2 Hz, CH$_2$OCO), 4.20 (4H, q, J = 7.1 Hz, OCH$_2$CH$_3$), 3.44 (4H, s, CH$_2$), 1.26 (6H, t, J = 7.1 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$, 50 MHz), δ: 166.58 (2C=O), 166.31 (2C=O), 156.36 (2C$_2$), 137.052, 134.40, 128.96, 126.12, 120.00, 117.10, 112.06, 111.07, 65.93 (2ArOCH$_2$), 63.70 (2CH$_2$O), 61.61 (2OCH$_2$CH$_3$), 41.45 (CH$_2$), 14.13 (2CH$_3$). MS *m/z* (%): 728 (M$^+$, 22), 614 (M$^+$ − COCH$_2$CO$_2$Et, 32), 500 (100). UV−vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 424 (4.53), 412 (sh, 4.10), 362 (4,31), 242 (4.73) nm.

9,10-Bis(4,5-dimethylthio-1,3-dithiol-2-ylidene)-2,6-bis-(1,4,8-trioxa-5,7-dioxodecyl)-9,10-dihydroanthracene (24b). 70% yield. Mp: 57−60 °C. Anal. (Calcd) for C$_{38}$H$_{40}$S$_8$O$_{10}$: C, 49.24 (50.00); H, 4.51 (4.62). FTIR (KBr): 2922, 2852, 1734

(C=O), 1603, 1560, 1541, 1498, 1458, 1412, 1369, 1147, 1097, 1032, 964, 810, 771 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz), δ: 7.44 (2H, d, $J_{3,4}$ = 8.5 Hz, ArH$_4$), 7.05 (2H, d, $J_{1,3}$ = 2.5 Hz, ArH$_1$), 6.82 (2H, dd, $J_{3,4}$ = 8.5 Hz, $J_{1,3}$ = 2.5 Hz, ArH$_3$), 4.5 (4H, t, J = 4.6 Hz, ArOCH$_2$), 4.24 (4H. t, J = 4.6 Hz, CH$_2$OCO), 4.20 (4H, q, J = 7.1 Hz, OCH$_2$CH$_3$), 3.44 (4H, s, CH$_2$), 2.38 (12H, s, SCH$_3$), 1.25 (6H, t, J = 7.1 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$, 50 MHz), δ: 166.49 (2C=O), 166.23 (2C=O), 156.54 (2C$_2$), 136.27, 129.73, 128.08, 126.59, 126.19, 125.31, 123.06, 111.98, 111.66, 65.83 (2ArOCH$_2$), 63.54 (2CH$_2$CO), 61.55 (2OCH$_2$CH$_3$), 41.39 (CH$_2$), 19.09 (2SCH$_3$), 18.96 (2SCH$_3$), 14.00 (2CH$_3$). MS *m/z* (%): 912 (M$^+$, 100). UV−vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 432 (4.38), 416 (sh, 4.32), 366 (4.17), 248 (4.66), 236 (sh, 4.58) nm.

9,10-Bis(1,3-dithiol-4,5-ethylenedithio-2-ylidene)-2,6-bis(1,4,8-trioxa-5,7-dioxodecyl)-9,10-dihydroanthracene (24c). 58% yield. Mp: 67−71 °C. Anal. (Calcd) for C$_{38}$H$_{36}$S$_8$O$_{10}$: C, 49.87 (50.22); H, 4.16 (3.96). FTIR (KBr): 2924, 2852, 1730 (C=O), 1686, 1603, 1560, 1508, 1452, 1406, 1369, 1273, 1217, 1147, 1097, 1026, 921, 791, 762, 748 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz), δ: 7.41 (2H, d, $J_{3,4}$ = 8.6 Hz, ArH$_4$), 7.02 (2H, d, $J_{1,3}$ = 2.4 Hz, ArH$_1$), 6.84 (2H, dd, $J_{3,4}$ = 8.6 Hz, $J_{1,3}$ = 2.4 Hz, ArH$_3$), 4.55 (4H, t, J = 4.4 Hz, ArOCH$_2$), 4.26 (4H, t, J = 4.4 Hz, CH$_2$OCO), 4.20 (4H, q, J = 7.1 Hz, OCH$_2$CH$_3$), 3.45 (4H, s, CH$_2$), 3.30 (4H, s, SCH$_2$), 3.29 (4H, s, SCH$_2$), 1.27 (6H, t, J = 7.1 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$, 50 MHz), δ: 166.56 (2C=O), 166.28 (2C=O), 156.54 (2C$_2$), 136.30, 128.52, 128.11, 126.77, 123.56, 111.98, 111.94, 110.90, 110.74, 65.92 (2ArOCH$_2$), 63.63 (2CH$_2$CO), 61.59 (2OCH$_2$CH$_3$), 41.43 (CH$_2$), 29.56 (2SCH$_2$), 29.54 (2SCH$_2$), 14.05 (2CH$_3$). MS *m/z* (%): 908 (M$^+$, 100). UV−vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 442 (4.05), 424 (sh, 3.96), 384 (3.76), 250 (4.32), 234 (4.31) nm.

Synthesis of Diads 26b,c and 28b,c. To a solution of C$_{60}$ (72 mg, 0.10 mmol), CBr$_4$ (33.2 mg, 0.10 mmol), and the malonate derivative (**23 or 24a−c**) (0.10 mmol) in toluene at 0 °C was added DBU (30 μL, 0.20 mmol) in *o*-DCB (1 mL). The reaction was monitored by TLC, and after 10−20 min, the reaction was stopped, since formation of products resulting from multiple addition was observed. Isolation and purification of products were achieved by column chromatography on silica gel first with toluene to elute the unreacted C$_{60}$ and then using toluene:ethyl acetate (50:1) as the eluent to separate the reaction products, which eluted in the order **25 or 27a−c** then **26a−c** and finally **28a−c**. Further purification was accomplished by three centrifugations using hexane, methanol, and ether as solvents.

Diad 26a. 22% yield. FTIR (KBr): 2963, 1747 (C=O), 1603, 1560, 1546, 1508, 1464, 1367, 1263, 1231, 1187, 1155, 1097, 1056, 862, 801, 657, 581, 526 cm^{-1}. ^{1}H NMR (CDCl$_3$/CS$_2$ 1:1, 300 MHz), δ: 7.52 (1H, d, $J_{3,4}$ = $J_{7,8}$ = 8.5 Hz, ArH$_4$ or ArH$_8$), 7.51 (1H, d, $J_{3,4}$ = $J_{7,8}$ = 8.5 Hz, ArH$_4$ or ArH$_8$), 7.15 (2H, d, $J_{1,3}$ = $J_{5,7}$ = 2.3 Hz, ArH$_1$, ArH$_5$), 6.76 (2H, dd, $J_{3,4}$ = $J_{7,8}$ = 8.5 Hz, $J_{1,3}$ = $J_{5,7}$ = 2.3 Hz, ArH$_3$, ArH$_7$), 6.28−6.26 (4H, m, CH=), 4.56−4.49 (4H, m, CH$_2$O), 4.40−4.38 (4H, m, OCH$_2$CH$_3$), 4.24−4.17 (4H, m, CH$_2$O), 3.40 (2H, s, CH$_2$), 1.47 (6H, t, J = 7.1 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$/CS$_2$ 1/1, 75 MHz), δ: 166.10 (C=O), 165.83 (C=O), 163.18 (C=O), 162.86 (C=O), 156.21 (C$_2$ or C$_6$), 156.04 (C$_2$ or C$_6$), 145.17, 145,12, 145.00, 144.98, 144.89, 144.69, 144.62, 144.45, 144.40, 144.20, 144.16, 143.66, 143.51, 142.81, 142.72, 142.67, 142.59, 142.02, 141.95, 141.55, 140.73, 140.71, 140.65, 139.33, 138.17, 138.12, 137.02, 136.85, 134.70, 134.60, 128.85, 128.76, 126.06, 121.39, 117.09, 111.88, 111.34, 111.19, 111.04, 77.21 (C$_{sp^3}$C$_{60}$), 71.22 (C$_{sp^3}$C$_{60}$), 65.72 (CH$_2$O), 65.07 (CH$_2$O), 63.52 (2CH$_2$O), 63.34 (CH$_2$O), 61.43 (CH$_2$O), 51.82 (C), 41.19 (CH$_2$), 14.20 (CH$_3$), 14.08 (CH$_3$). MS *m/z* (%): 1470 (M$^+$ + Na, 60). UV−vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 426 (4.38), 410 (sh, 4.37), 362 (4.47), 324 (4.63), 254 (5.11) nm.

Diad 26b. 13% yield. FTIR (KBr): 2918, 1745 (C=O), 1601, 1536, 1496, 1461, 1425, 1367, 1226, 1098, 1058, 1024, 953, 752, 525 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz), δ: 7.38 (1H, d, $J_{3,4}$ = $J_{7,8}$ = 8.5 Hz, ArH$_4$ or ArH$_8$), 7.37 (1H, d, $J_{3,4}$ = $J_{7,8}$ = 8.5 Hz, ArH$_4$ or ArH$_8$), 6.99 (1H, d, $J_{1,3}$ = $J_{5,7}$ = 2.3 Hz, ArH$_1$ or ArH$_5$), 6.98 (1H, d, $J_{1,3}$ = $J_{5,7}$ = 2.3 Hz, ArH$_1$ or ArH$_5$), 6.78 (2H, dd,

$J_{3,4} = J_{7,8} = 8.5$ Hz, $J_{1,3} = J_{5,7} = 2.3$ Hz, ArH$_3$, ArH$_7$), 4.54–4.52 (4H, m, OCH$_2$), 4.42–4.38 (4H, m, OCH$_2$CH$_3$), 4.23–4.18 (4H, m, CH$_2$O), 3.47–3.44 (2H, m, CH$_2$), 2.39 (12H, s, SCH$_3$), 1.47 (3H, t, $J = 7.1$ Hz, CH$_3$), 1.28 (3H, t, $J = 7.1$ Hz, CH$_3$). ^{13}C NMR (CDCl$_3$, 75 MHz), δ: 166.31 (C=O), 166.03 (C=O), 163.41 (C=O), 163.07 (C=O), 156.53 (C$_2$ or C$_6$), 156.39 (C$_2$ or C$_6$), 145.21, 145.18, 145.07, 145.00, 144.96, 144.99, 144.80, 144.69, 144.66, 144.51, 144.46, 144.41, 144.25, 144.16, 144.13, 143.72, 143.52, 143.50, 142.76, 142.72, 142.69, 142.67, 142.62, 142.56, 142.11, 142.05, 141.99, 141.61, 141.57, 141.51, 140.75, 140.71, 139.42, 138.11, 138.05, 136.43, 136.21, 130.41, 130.13, 130.11, 130.00, 129.98, 128.06, 128.00, 127.97, 127.56, 126.63, 126.37, 126.11, 126.00, 125.82, 125.38, 123.16, 123.14, 122.98, 122.88, 122.86, 111.93, 111.78, 111.47, 77.20 (C$_{sp^3}$C$_{60}$), 71.25 (C$_{sp^3}$C$_{60}$), 65.78 (CH$_2$O), 65.11 (CH$_2$O), 63.52 (CH$_2$O), 63.43 (CH$_2$O), 61.54 (2CH$_2$O), 51.86 (C), 41.29 (CH$_2$), 19.20 (CH$_3$S), 19.16 (SCH$_3$), 19.13 (SCH$_3$), 19.03 (SCH$_3$),14.21 (CH$_3$), 14.08 (CH$_3$). MS m/z (%): 1632 (M$^+$, 100). UV–vis (CH$_2$Cl$_2$) $λ_{max}$ (log ε): 430 (4.35), 414 (sh, 4.31), 362 (4.44), 321 (4.60), 254 (5.08) nm.

Diad 26c. 12% yield. FTIR (KBr): 2957, 2924, 1747 (C=O), 1601, 1558, 1511, 1457, 1414, 1370, 1287, 1229, 1100, 1057, 1023, 812, 527 cm^{-1}. ^{1}H NMR (CDCl$_3$/CS$_2$, 2/1, 300 MHz), δ: 7.33 (1H, d, $J_{3,4} = J_{7,8} = 8.3$ Hz, ArH$_4$ or ArH$_8$), 7.32 (1H, d, $J_{3,4} = J_{7,8} = 8.3$ Hz, ArH$_4$ or ArH$_8$), 6.94 (2H, d, $J_{1,3} = J_{5,7} = 2.5$ Hz, ArH$_1$, ArH$_5$), 6.77 (1H, dd, $J_{3,4} = J_{7,8} = 8.3$ Hz, $J_{1,3} = J_{5,7} = 2.5$ Hz, ArH$_3$ or ArH$_7$), 6.74 (1H, dd, $J_1 = 8.3$ Hz, $J_2 = 2.5$ Hz, ArH$_3$ or ArH$_7$), 4.56–4.17 (12H, m, OCH$_2$), 3.44 (2H, s, CH$_2$), 3.33–3.27 (8H, m, SCH$_2$), 1.49 (3H, t, $J = 7.1$ Hz, CH$_3$), 1.28 (3H, t, $J = 7.1$ Hz, CH$_3$). ^{13}C NMR (CDCl$_3$/CS$_2$, 2/1, 75 MHz), δ: 166.18 (C=O), 166.89 (C=O), 163.37 (C=O), 163.07 (C=O), 156.52 (C$_2$ or C$_6$), 156.28 (C$_2$ or C$_6$), 147.70, 145.72, 145.18, 145.00, 144.94, 144.83, 144.70, 144.64, 144.50, 144.39, 144.28, 144.15, 144.03, 144.93, 143.69, 143.61, 143.60, 143.59, 143.31, 142.73, 142.63, 142.25, 142.10, 141.96, 141.63, 141.55, 141.17, 140.84, 140.68, 139.60, 139.40, 138.05, 136.41, 136.28, 136.22, 128.78, 128.13, 128.07, 128.01, 126.72, 126.63, 122.99, 111.90, 111.84, 111.80, 111.76, 111.08, 111.01, 110.92, 77.20 (C$_{sp^3}$C$_{60}$), 71.23 (C$_{sp^3}$C$_{60}$), 65.78 (2CH$_2$O), 63.52 (2CH$_2$O), 63.36 (CH$_2$O), 61.47 (CH$_2$O), 51.82 (C), 41.23 (CH$_2$), 29.72 (SCH$_2$), 14.09 (CH$_3$). MS m/z (%): 1651 (M$^+$ + Na, 100), 1628 (M$^+$). UV–vis (CH$_2$Cl$_2$) $λ_{max}$ (log ε): 444 (5.51), 426 (sh, 4.30), 376 (4.31), 316 (sh, 4.62), 252 (5.05) nm.

Diad 28b (Regioisomeric Mixture). 8% yield. FTIR (KBr): 2923, 2853, 1745 (C=O), 1668, 1591, 1557, 1495, 1460, 1426, 1367, 1287, 1226, 1172, 1101, 1057, 962, 860, 808, 750, 525 (C$_{60}$) cm^{-1}. ^{1}H NMR (CDCl$_3$/CS$_2$, 2/1, 300 MHz), δ: 6.96–6.57 (6H, m, ArH), 5.0–4.2 (12H, m, CH$_2$), 1.64–1.55 (6H, m, CH$_3$). MS m/z (%): 1644 (M$^+$ + O, 25). UV–vis (CH$_2$Cl$_2$) $λ_{max}$ (log ε): 430 (4.33), 414 (sh, 4.30), 366 (4.46), 318 (sh, 4.62), 250 (4.64) nm.

Diad 28c (Regioisomeric Mixture). 6% yield. FTIR (KBr): 2955, 2923, 2851, 1747 (C=O), 1603, 1559, 1508, 1456, 1378, 1286, 1230, 1172, 1098, 1062, 1028, 862, 764, 706, 547, 526 cm^{-1}. MS m/z (%): 1649 (M$^+$ + Na, 100). UV–vis (CH$_2$-Cl$_2$) $λ_{max}$ (log ε): 442 (4.99), 376 (4.23), 248 (4.18) nm.

Synthesis of Triads 25 and 27a–c. To a solution of C$_{60}$ (432 mg, 0.60 mmol), CBr$_4$ (99.6 mg, 0.30 mmol), and the dimalonate derivative (**23** or **24a–c**) (0.10 mmol) in toluene at 0 °C was added DBU (60 μL, 0.40 mmol) in *o*-DCB (1 mL) was added. The reaction was monitored by TLC, and after 10–30 min, the reaction was stopped, since formation of many addition products to C$_{60}$ was observed. Purification of products was achieved by column chromatography on silica gel, first with toluene to elute the unreacted C$_{60}$ and then using toluene: ethyl acetate (50:1) as the eluent. Further purification was accomplished by three centrifugations using hexane, methanol, and ethyl ether as solvents, respectively.

Triad 25. 8% yield. FTIR (KBr): 2961, 2920, 2852, 1741 (C=O), 1600, 1531, 1491, 1462, 1416, 1371, 1261, 1229, 1198, 1095, 1020, 960, 801, 702, 877, 526 cm^{-1}. ^{1}H NMR (CDCl$_3$/CS$_2$ 1:1, 300 MHz), δ: 7.60 (2H, d, $J_{3,4} = 8.4$ Hz, ArH$_4$), 7.00

(2H, d, $J_{1,3} = 2.2$ Hz, ArH$_1$), 6.78 (2H, dd, $J_{3,4} = 8.4$ Hz, $J_{1,3} = 2.2$ Hz, ArH$_3$), 4.69 (4H, q, $J = 7.1$ Hz, OCH$_2$), 2.43–2.37 (12H, m, SCH$_3$), 1.63 (6H, t, $J = 7.1$ Hz, CH$_3$). ^{13}C NMR (CDCl$_3$/CS$_2$ 1/1, 75 MHz), δ: 162.90 (4C=O), 154.12 (2C$_2$), 148.03, 145.40, 145.31, 145.19, 145.15, 145.08, 145.05, 145.02, 144.86, 144.77, 144.64, 144.57, 144.53, 144.27, 143.80, 143.74, 143.70, 142.98, 142.95, 142.90, 142.78, 142.76, 142.09, 141.93, 141.64, 140.97, 140.87, 139.98, 138.10, 136.29, 136.05, 127.29, 127.23, 126.82, 126.34, 126.25, 125.90, 122.48, 118.35, 118.17, 113.18, 113.09, 112.38, 77.21 (C$_{sp^3}$C$_{60}$), 71.26 (C$_{sp^3}$C$_{60}$), 63.58 (CH$_2$O), 65.06 (CH$_2$O), 51.00 (2C), 19.35 (2SCH$_3$), 19.13 (2SCH$_3$), 14.40 (CH$_3$), 14.20 (CH$_3$). MS m/z (%): 1542 (M$^+$ − C$_{60}$, 30), 822 (M$^+$ − 2C$_{60}$, 4). UV–vis (CH$_2$Cl$_2$) $λ_{max}$ (log ε): 439 (4.13), 362 (sh, 4.19), 324 (4.42), 255 (4.92), 236 (sh, 4.87) nm.

Triad 27a. 13% yield. FTIR (KBr): 2953, 2923, 2853, 1746 (C=O), 1650, 1601, 1546, 1514, 1458, 1431, 1370, 1232, 1209, 1182, 1098, 1058, 1019, 639, 526 cm^{-1}. ^{1}H NMR (CDCl$_3$/CS$_2$ 1/1, 300 MHz), δ: 7.48 (2H, d, $J_{3,4} = 8.6$ Hz, ArH$_4$), 7.10 (2H, d, $J_{1,3} = 2.5$ Hz, ArH$_1$), 6.73 (2H, dd, $J_{3,4} = 8.6$ Hz, $J_{1,3} = 2.5$ Hz, ArH$_3$), 6.26 (4H, s, CH=), 4.89–4.88 (4H, m, CH$_2$O), 4.48 (4H, q, $J = 7.1$ Hz, OCH$_2$CH$_3$), 4.39–4.38 (4H, m, CH$_2$O), 1.49 (6H, t, $J = 7.1$ Hz, CH$_3$). ^{13}C NMR (CDCl$_3$/CS$_2$ 1/ 1, 75 MHz,), δ: 163.22 (2C=O), 162.90 (2C=O), 156.07 (2C$_2$), 145.23, 145.19, 145.04, 144.94, 144.85, 144.73, 144.66, 144.50, 144.45, 144.29, 144.22, 143.70, 143.56, 142.85, 142.76, 142.71, 142.65, 142.61, 142.05, 141.99, 141.59, 140.78, 140.68, 139.38, 138.23, 138.16, 137.00, 134.72, 128.87, 126.13, 125.18, 121.31, 117.16, 111.46, 111.34, 77.20 (C$_{sp^3}$C$_{60}$), 71.26 (C$_{sp^3}$C$_{60}$), 65.68 (2CH$_2$O), 65.06 (2CH$_2$O), 63.36 (2CH$_2$O), 51.36 (2C), 14.25 (2CH$_3$). MS m/z (%): 2166 (M$^+$, 5), 1446 (M$^+$ − C$_{60}$, 100), 721 (C$_{60}$ + H, 10). UV–vis (CH$_2$Cl$_2$) $λ_{max}$ (log ε): 426 (3.96), 406 (sh, 3.96), 364 (sh, 4.16), 326 (4.42), 258 (5.05) nm.

Triad 27b. 15% yield. FTIR (KBr): 2922, 2856, 1741 (C=O), 1599, 1556, 1493, 1461, 1420, 1265, 1228, 1204, 1054, 951, 525 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz), δ: 7.35 (2H, d, $J_{3,4} = 8.6$ Hz, ArH$_4$), 6.96 (2H, d, $J_{1,3} = 2.3$ Hz, ArH$_1$), 6.75 (2H, dd, $J_{3,4} = 8.6$ Hz, $J_{1,3} = 2.3$ Hz, ArH$_3$), 4.95–4.87 (4H, m, OCH$_2$), 4.57 (4H, q, $J = 7.1$ Hz, OCH$_2$CH$_3$), 4.39–4.37 (4H, m, CH$_2$O), 2.37 (12H, s, SCH$_3$), 1.50 (6H, t, $J = 7.1$ Hz, CH$_3$). ^{13}C NMR (CDCl$_3$, 50 MHz), δ: 163.71 (2C=O), 163.38 (2C=O), 156.46 (2C$_2$), 145.41, 145.17, 145.08, 145.06, 145.03, 144.91, 144.81, 144.79, 144.77, 144.74, 144.72, 144.63, 144.57, 144.55, 144.40, 144.26, 143.83, 143.61, 142.98, 142.89, 142.87, 142.82, 142.77, 142.72, 142.66, 142.23, 142.18, 142.09, 141.75, 141.72, 141.70, 141.65, 140.88, 140.80, 140.79, 140.77, 139.65, 138.11, 138.06, 136.52, 129.85, 129.01, 128.22, 128.10, 127.78, 127.45, 126.66, 126.11, 125.93, 122.48, 112.62, 112.13, 77.19 (C$_{sp^3}$C$_{60}$), 71.39 (C$_{sp^3}$C$_{60}$), 65.89 (2CH$_2$O), 65.18 (2CH$_2$O), 63.61 (2CH$_2$O), 52.00 (2C), 19.16 (2SCH$_3$), 19.06 (2SCH$_3$), 14.30 (CH$_3$), 14.11 (CH$_3$). MS m/z (%): 2350 (M$^+$, 90), 1629 (M$^+$ − C$_{60}$, 10). UV–vis (CH$_2$Cl$_2$) $λ_{max}$ (log ε): 428 (3.97), 414 (sh, 3.95), 366 (sh, 4.18), 326 (4.46), 256 (4.94) nm.

Triad 27c. 12% yield. FTIR (KBr): 2955, 2921, 2850, 1744 (C=O), 1672, 1592, 1559, 1456, 1436, 1323, 1291, 1230, 1204, 1156, 1139, 1119, 1097, 1061, 721, 694, 526 cm^{-1}. ^{1}H NMR (CDCl$_3$/CS$_2$, 1/1, 300 MHz), δ: 7.68 (2H, d, $J_{3,4} = 8.2$ Hz, ArH$_4$), 6.88 (2H, d, $J_{1,3} = 2.5$ Hz, ArH$_1$), 6.71 (2H, dd, $J_{3,4} = 8.2$ Hz, $J_{1,3} = 2.5$ Hz, ArH$_3$), 4.93–4.83 (4H, m, OCH$_2$), 4.55 (4H, q, $J = 7.1$ Hz, OCH$_2$CH$_3$), 4.37–4.29 (4H, m, CH$_2$O), 3.30–3.26 (8H, m, SCH$_2$), 1.50 (6H, t, $J = 7.1$ Hz, CH$_3$). ^{13}C NMR (CDCl$_3$/CS$_2$, 1/1, 75 MHz), δ: 163.07 (C=O), 163.05 (C=O), 162.68 (C=O), 156.13 (2C$_2$), 136.30, 145.12, 145.10, 144.92, 144.85, 144.76, 144.64, 144.56, 144.44, 144.40, 144.36, 144.31, 144.19, 144.08, 143.62, 143.61, 143.58, 143.55, 143.53, 142.86, 142.74, 142.67, 142.56, 142.55, 142.04, 141.89, 141.56, 141.54, 141.47, 140.78, 140.74, 140.60, 139.30, 138.04, 136.25, 133.39, 128.88, 128.82, 128.54, 128.16, 128.12, 128.05, 128.03, 128.01, 126.64, 126.61, 126.56, 126.53, 126.51, 122.64, 111.90, 111.35, 111.33, 110.98, 77.21 (C$_{sp^3}$C$_{60}$), 71.15 (C$_{sp^3}$C$_{60}$), 65.64 (2CH$_2$O), 64.84 (2CH$_2$O), 63.22 (2CH$_2$O), 51.73 (2C), 30.40 (SCH$_2$), 29.81 (2SCH$_2$), 29.78 (SCH$_2$), 14.24 (2CH$_3$). UV–vis (CH$_2$Cl$_2$) $λ_{max}$ (log ε): 446 (4.07), 428 (sh, 4.06), 322 (4.59), 254 (5.05) nm.

Supporting Information Available: Synthetic procedures and experimental data for **6**, **8a**−**c**, **9a**−**c**, **10a**−**c**, **11a**, **15**−**19**, **20a**−**c**, **21**, and **22a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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