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# Dihydroazulene–Buckminsterfullerene Conjugates

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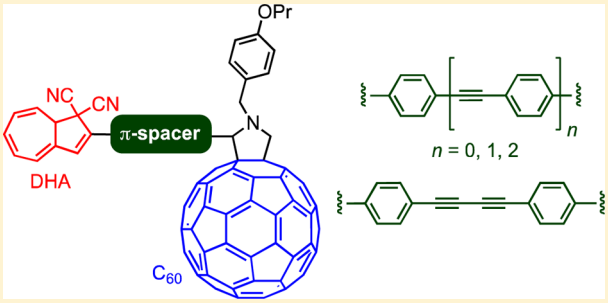
Supporting Information

**ABSTRACT:** The dihydroazulene (DHA)/vinylheptafulvene (VHF) photo/thermoswitch has recently attracted interest as a molecular switch for molecular electronics. In this field, Buckminsterfullerene, $C_{60}$, has been shown to be a useful anchoring group for adhering a molecular wire to an electrode. Here we have combined the two units with the overall aim to elucidate how $C_{60}$ influences the DHA–VHF switching events. Efficient synthetic protocols for making covalently linked DHA-$C_{60}$ conjugates were developed, using Prato, Sonogashira, Hay, and Cadiot–Chodkiewicz reactions. These syntheses provide as well a variety of potentially useful DHA and $C_{60}$ building blocks for acetylenic scaffolding. The two units were separated by bridges of various lengths, such as oligo(phenyleneethynylene) (OPE2 and OPE3) wires. The distance of separation was found to influence strongly the light-induced ring-opening reaction of DHA to its corresponding VHF. Thus, $C_{60}$ was found to significantly quench this conversion when situated closely to the DHA unit.




## INTRODUCTION

Molecules that change their single-molecule conductivity upon an external stimulus are interesting as components for molecular electronics devices.[1] Light is a particularly attractive stimulus for triggering such conductivity changes, and several molecular electronics studies have in recent years focused on photoswitches such as dithienylethenes[2] and azobenzenes.[3] Recently it was shown that derivatives of dihydroazulene (DHA) can also be employed for light-triggered conductance switching in single-molecule devices.[4] DHA undergoes a 10-electron retro-electrocyclization upon irradiation to furnish a vinylheptafulvene (VHF), which can exist as s-*cis* and s-*trans* conformers (Scheme 1).[5] When VHF is in its s-*cis* conformation, it can undergo a thermally induced ring closure to regenerate DHA. Starting from either acetophenone or *p*-iodoacetophenone, derivatives **1**[6] and **2**[7] with a phenyl or *p*-iodophenyl at position 2 are readily prepared in few steps on a large scale.

Much work in the field of molecular electronics has also focused on the nontrivial contacting of the molecule to an electrode. In particular, thiolate end groups[8] have been employed as anchoring groups ("molecular alligator clips") as these groups adhere well to gold. Recently, however, Buckminsterfullerene, $C_{60}$, was successfully employed as an anchoring group, providing a well-defined contact region to gold.[9] Moreover, several synthetic protocols have been devised for preparing molecular wires with $C_{60}$ end caps,[10] typically employing a [3 + 2] dipolar cyclization (Prato reaction[11]) or an acetylide addition reaction.[10a] Stimulated by the DHA–VHF conductance switching and the beneficial molecular wiring via $C_{60}$ anchoring, we became interested to link these two entities together. Here we present synthetic protocols for obtaining such DHA-$C_{60}$ conjugates in which the distance between the DHA and $C_{60}$ is varied in a systematic manner, using rigid and $\pi$-conjugated linkers (Chart 1). Indeed, this distance was found to influence strongly the light-induced ring-opening of the DHA unit; at close distances, the light-induced ring-opening reaction occurred less readily. Compounds **3a**/**b**–**5** were prepared by a Prato reaction in the final step using DHA precursors with an incorporated aldehyde functionality. In

**Scheme 1**

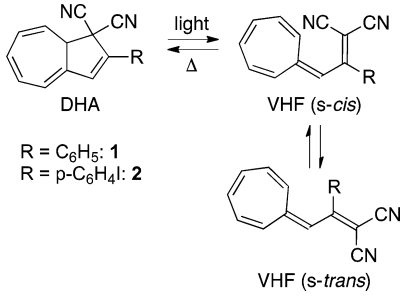



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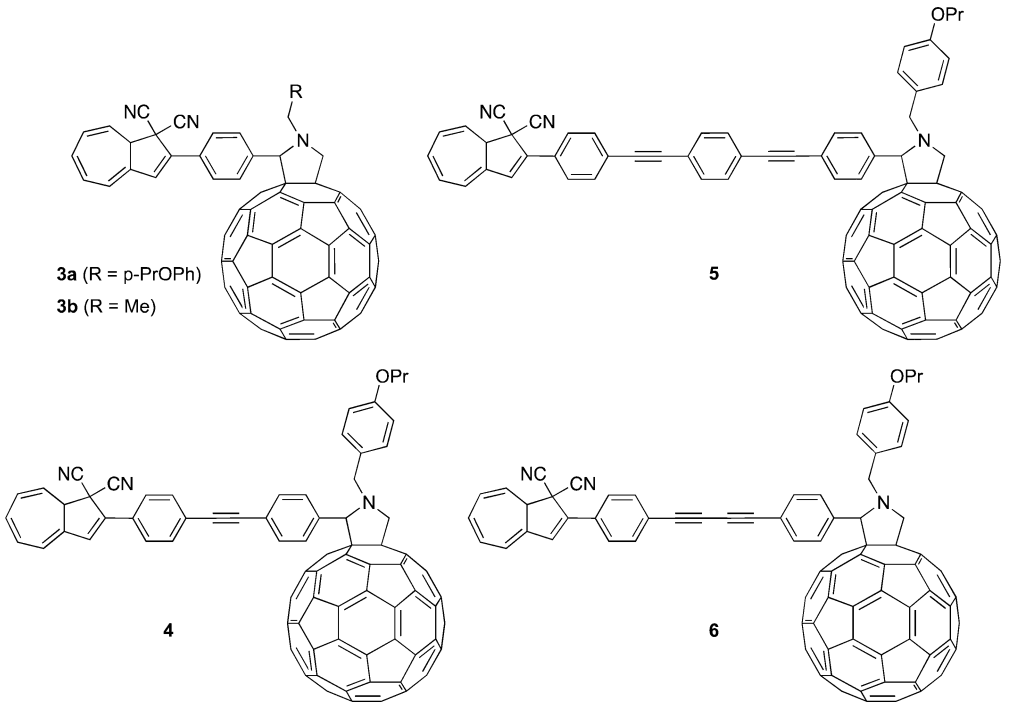
**Chart 1**



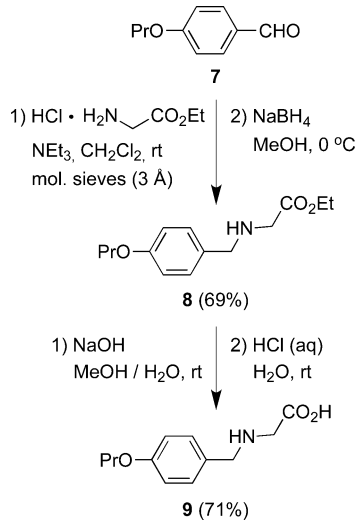

addition, we have devised a route to compound **4** via a final Sonogashira cross-coupling[12] reaction. Compound **6** was made by an unsymmetrical Hay coupling[13] from the corresponding alkyne precursors as well as by a palladium-catalyzed version of the Cadiot–Chodkiewicz cross-coupling[14] from terminal alkyne and bromoalkyne precursors. The central conjugated part separating the DHA and $C_{60}$ cores in compounds **4** and **5** is an oligo(phenyleneethynylene), OPE2 and OPE3, respectively. This is noteworthy in view of the fact that OPEs have been explored considerably as molecular wires for molecular electronics.[8,15] The design of $C_{60}$ conjugates usually has to take into consideration the poor solubility of such compounds. This can be addressed by the introduction of solubilizing groups upon the nitrogen atom of the pyrrolidine ring using tailor-made amino acids in the Prato reaction. The propyloxybenzyl substituent was chosen to provide solubility of the products; hexyloxybenzyl has previously been used with success for this purpose, and in addition, its use has shown short reaction times with decent conversion.[16] One conjugate (**3b**) without this group was, however, also prepared and studied to support the quenching effect exerted by $C_{60}$.

## RESULTS AND DISCUSSION

**Synthesis.** Our first objective was to develop a synthetic route for DHA-$C_{60}$ conjugates based on a final Prato reaction between an aldehyde, a glycine derivative, and $C_{60}$. First, glycine was functionalized with the propyloxybenzyl substituent. Thus, the known 4-propyloxybenzaldehyde (**7**[17]) was treated with glycine ethylester hydrochloride, and the intermediate imine was reduced with sodium borohydride to furnish compound **8** (Scheme 2). The ester functionality was then hydrolyzed, and the glycine derivative **9** was isolated as a fluffy solid at pH 6.7.

Synthesis of the DHA-aldehyde precursor for conjugates **3a** and **3b** is shown in Scheme 3. The acetophenone **10** was subjected to a Knoevenagel condensation with malononitrile to furnish the product **11**, in the presence of hexamethyldisilazane

**Scheme 2**




(HMDS) and AcOH (Knoevenagel conditions of Barnes et al.[18]). Treatment with tropylium tetrafluoroborate ($C_7H_7^+BF_4^-$) in the presence of triethylamine as base gave a mixture of products **12a**/**b**. Subjecting this mixture to tritylium tetrafluoroborate ($Ph_3C^+BF_4^-$) followed by triethylamine generated an intermediate VHF that was thermally converted to DHA **13**.[19] Reduction of the ester group by the action of DIBAL-H finally generated the aldehyde **14**, which was, however, difficult to obtain analytically pure due to instability (required repeated column chromatography). The low yield also reflects the fact that side reactions were clearly evident during the progress of the reaction. Subjecting the compound to Prato reactions using either **9** or *N*-ethylglycine furnished DHA-$C_{60}$ conjugates **3a** and **3b** (Scheme 3).

Next, conjugates **4** and **5** were targeted. The known iodo-DHA **2**[7] was subjected to Sonogashira cross-couplings with the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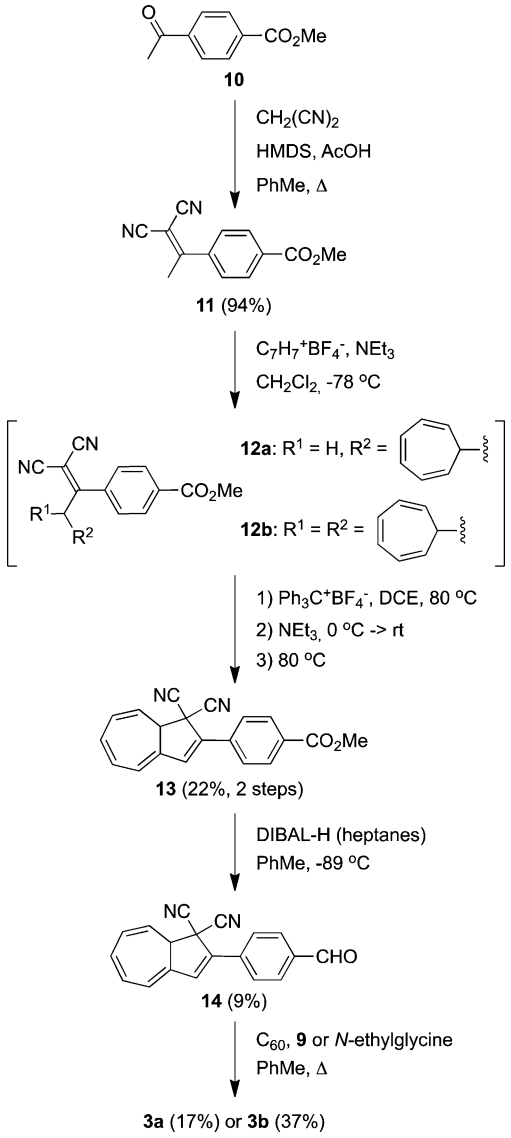
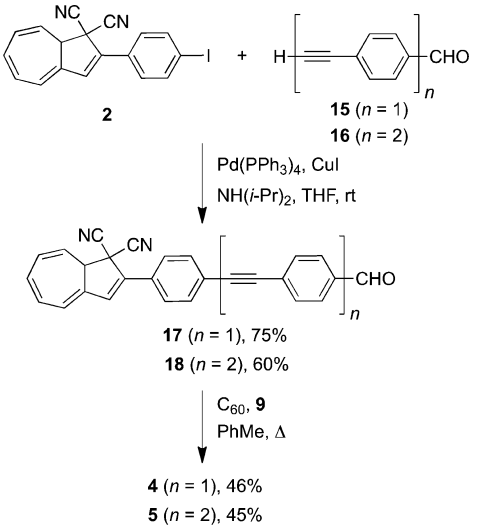
**Scheme 3**




**Scheme 4**




known alkynes **15** and **16**,[10g] respectively, to provide the DHA-aldehydes **17** and **18** (Scheme 4). Single crystals of **17** were grown from chloroform and subjected to X-ray crystallographic analysis, confirming the structure (Figure S1, Supporting Information). Finally, a Prato reaction between $C_{60}$, the glycine derivative **9**, and each of the DHA-aldehydes **17** and **18** provided the DHA-$C_{60}$ conjugates **4** and **5** (Scheme 4).

All DHA-$C_{60}$ conjugates exhibited good solubility in organic solvents and were isolated by column chromatography while shielding the column from light to avoid conversions to VHFs. They all contained two stereocenters (position 8a in DHA and position 2 in pyrrolidine) and were isolated as mixtures of diastereoisomers. The functionalization of the fullerene in each conjugate product was supported by spectroscopy. For example, $^1$H NMR of these fullerene-DHA hybrids gave rise to the observance of characteristic pattern for a 2-substituted fulleropyrrolidine in addition to being superimposed onto/accompanying a typical DHA spectrum. This consisted of a single resonance for the pyrrolidine CH proton at $\delta$ 5.2 ppm and two doublets for the inequivalent methylene protons around $\delta$ 4.9 and 4.2 ppm ($J$ = 9.4 Hz). In addition, all fullerene derivatives bearing the propyloxybenzyl solubilizing group also exhibited an AB system of the benzyl $CH_2$ protons around $\delta$ 4.5 and 3.7 ppm ($J$ = 13.2 Hz). Although two chiral centers are present in all of these products (position C-8a in DHA and the methylene carbon in pyrrolidine), doubling of the signals due to diastereoisomerism was noticed only when the two centers were closer in proximity (compounds **3a** and **3b**).

The next objective was to employ Sonogashira or Hay reactions to link the units together by acetylenic scaffolding. Only few reports on metal-catalyzed coupling reactions on suitable $C_{60}$ derivatives are known in the literature.[20] For this purpose, $C_{60}$ derivatives with iodophenyl or alkyne functional groups were targeted. Thus, a Prato reaction between either 4-iodobenzaldehyde (**19**) or 4-ethynylbenzaldehyde (**20**) and **9** and $C_{60}$ provided the important building blocks **21** and **22** (Scheme 5). Gratifyingly, the iodide **21** underwent a Sonogashira cross-coupling with trimethylsilylacetylene to furnish compound **23**. A DHA incorporating an ethynyl group was therefore targeted as the next coupling partner. This functionalization can be accomplished employing two routes. In the route presented in Scheme 6, the iodo-DHA **2** was treated with triisopropylsilylacetylene under Sonogashira conditions to provide compound **24**. Desilylation was accomplished using tetrabutylammonium fluoride, furnishing the terminal alkyne product **25** in a yield of 76%. The reaction had to be carried out under acidic conditions (to avoid azulene formation[21]) and was rather slow as it required reflux for 16 h in order to reach completion. In an alternative attempt, we converted the DHA into VHF using aluminum chloride (according to a procedure reported recently[22]) and then subjected this compound to the fluoride source in the absence of acid as VHF is not base-sensitive. However, after 24 h during which the mixture was irradiated, TLC indicated no formation of the terminal alkyne. As the trimethylsilyl group is easier to cleave, we also prepared the corresponding trimethylsilylethynyl-DHA, but the purification of this compound was tedious, and we could not separate it from a byproduct formed under the reaction conditions. Instead, an alternative route was developed (Scheme 7), in which the alkyne functionality was incorporated early in the synthesis before the DHA core is constructed. Following analogous procedures for making **1** and **2**,[6,7] the ketone **26**[23] was first subjected to a Knoevenagel condensation with malononitrile to give compound **27**. This compound was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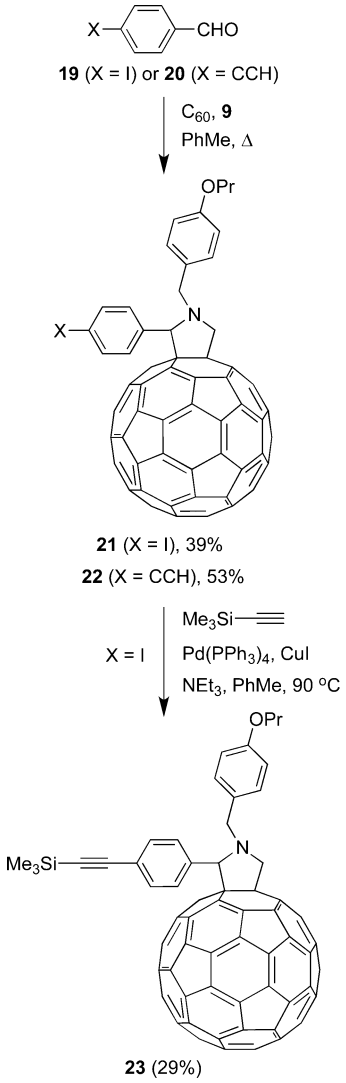
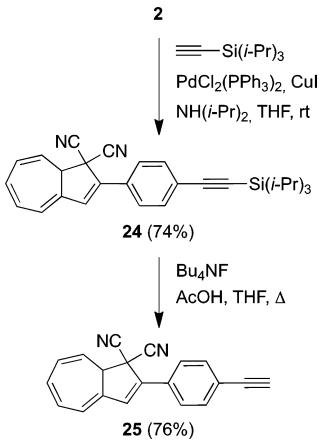
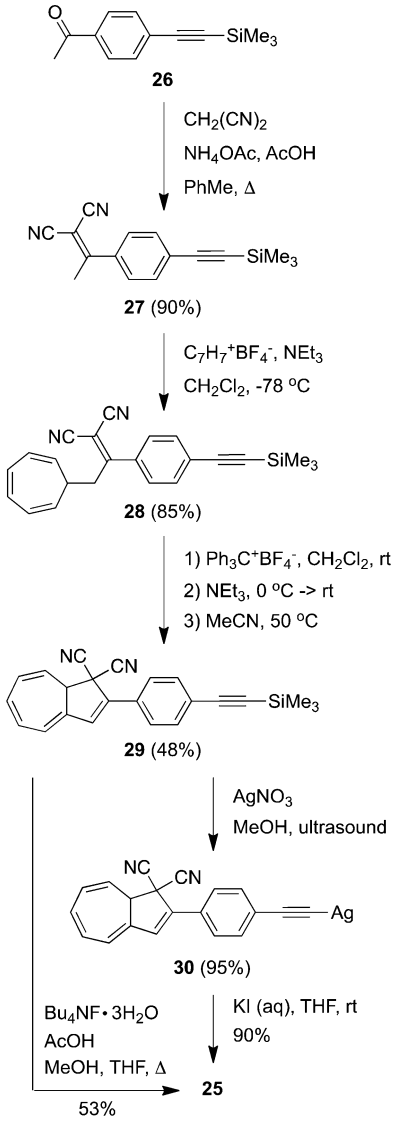
**Scheme 5**




**Scheme 6**




**Scheme 7**




then treated with tropylium tetrafluoroborate ($C_7H_7^+BF_4^-$) in the presence of triethylamine as base to furnish the product **28**. Hydride abstraction by the action of tritylium tetrafluoroborate ($Ph_3C^+BF_4^-$) followed by proton abstraction by triethylamine generated the intermediate VHF that was thermally converted to the DHA product **29**. Desilylation could now be completed upon treatment with tetrabutylammonium fluoride under acidic conditions within 16 h at room temperature to provide the terminal alkyne **25** in a yield of 53%. The yield of desilylation could, however, be improved by another method. Thus, treatment with silver nitrate in methanol generated the silver-acetylide intermediate **30** that could be isolated as a yellow solid (**CAUTION**: silver-acetylides are potentially explosive). Subsequent treatment with a saturated aqueous solution of potassium iodide then provided **25** in an overall yield of 86% from **29**. With the new building blocks at hand, metal-catalyzed coupling reactions were attempted. Indeed, the iodide **21** and the alkyne **25** were successfully coupled together under Sonogashira conditions affording the conjugate **4** (Scheme 8). Moreover, the two terminal alkynes **22** and **25** were coupled together under oxidative Hay conditions (using chlorobenzene as solvent[20e]) (Scheme 9) to furnish the butadiyne-bridged conjugate **6** (together with homocoupled byproduct of each starting material; the homocoupling products are not a point of discussion here as this is the subject of a separate investigation). This compound can also be prepared by a palladium-catalyzed version of the Cadiot–Chodkiewicz cross-coupling (Scheme 9). First, the bromoalkyne **31** (of limited stability) was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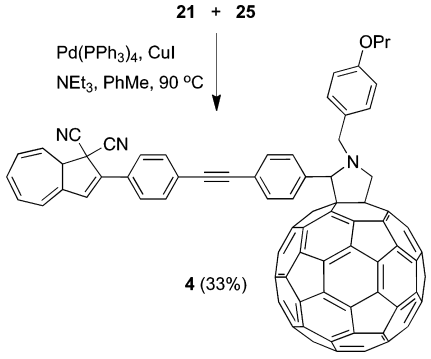
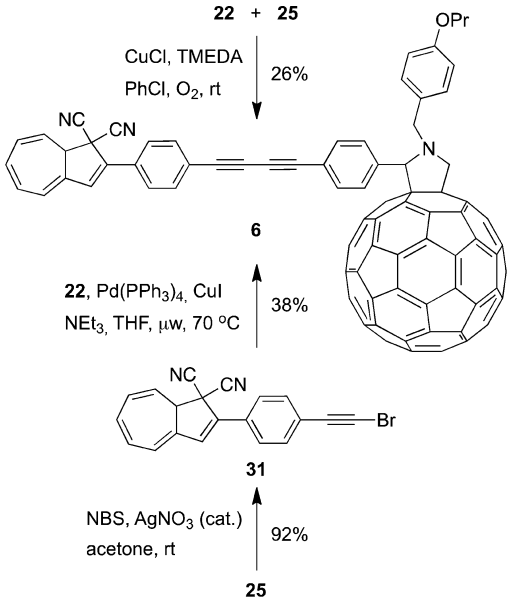
**Scheme 8**




**Scheme 9**




prepared in high yield by treating the DHA **25** with *N*-bromosuccinimide (NBS) and $AgNO_3$. Next, treating it with the alkyne **22** and the $Pd(PPh_3)_4$/CuI catalyst system at room temperature did not provide any of the product **6** according to TLC inspection; only products corresponding to homocoupling of **22** (in a trace amount) and debromination of **31** were observed. However, subjecting the reaction mixture to microwave heating (70 °C) resulted in formation of the product **6**, which was isolated in a yield of 38% after column chromatographic purification (the product of homocoupling of **22** was also isolated as a byproduct). The yield from the Cadiot–Chodkiewicz reaction is thus slightly higher than that obtained from the Hay reaction, but on the other hand, it includes one additional step, namely, synthesis of the bromoalkyne precursor.

The structures described above have the DHA and $C_{60}$ units covalently linked together. It is also interesting to elucidate how the units would interact by noncovalent interactions. We managed to grow crystals of the iodo-DHA **2** and $C_{60}$ from $CS_2/CH_2Cl_2$. X-ray crystallographic analysis revealed a 2:1 complex in the solid state (Figure 1). In the structure, the iodo-DHA molecules are sandwiched between hexagonal close-packed (hcp) layers of $C_{60}$ molecules. Each iodo-DHA molecule lies above a hollow in the hcp $C_{60}$ layer, with one of its cyano groups pointing directly into the center of the

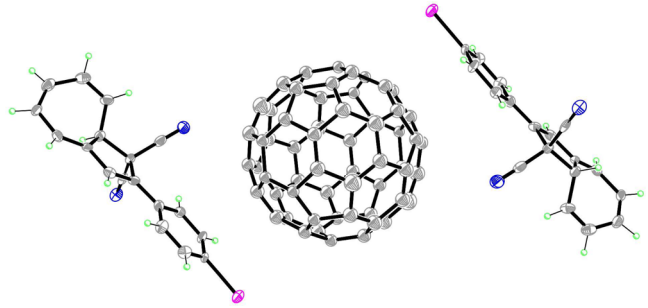


**Figure 1.** 2:1 Complex between DHA **2** and $C_{60}$ (with displacement ellipsoids at 50% probability for non-H atoms). CCDC 886632.

trigonal space. The other cyano group points across the face of one $C_{60}$ molecule, forming a contact of ca. 3.19 Å between the terminal N atom and the centroid of one benzene ring. The plane of the iodophenyl ring forms a $\pi-\pi$ interaction with another $C_{60}$ molecule, with an interplanar separation of ca. 3.15 Å. The I atom points toward a third $C_{60}$ molecule, with a shortest I···C contact of ca. 3.45 Å.

**Spectroscopy and Switching Studies.** All five DHA-$C_{60}$ complexes **3a**, **3b**, **4**, **5**, and **6** as well as the two OPE aldehydes **17** and **18** could be converted to their corresponding VHFs upon irradiation. The absorption maxima are listed in Table 1, and the absorption spectra of DHA **3a** and its corresponding VHF are shown in Figure 2 as representative examples. It should be noted that the characteristic DHA absorption, usually found around 350 nm,[6] is overlapping with the absorption of the $C_{60}$ moiety. The fullerene substituent was found to have little influence on the thermally induced ring closure of VHF to DHA as revealed by the rate constants and half-lives at 50 °C listed in Table 1. The OPE bridges exert themselves a rate-enhancing effect (as expected for an electron-withdrawing group at this position[21,24]), while the presence of $C_{60}$ causes only small changes. Thus, VHFs corresponding to DHAs **4** and **17** behave rather similarly as do VHFs corresponding to DHAs **5** and **18**.

The photoresponses of the DHAs were studied in 1,2-dichloroethane at the same wavelength of irradiation (351 nm). A 1:1 sample of DHA **1** and $C_{60}$-derivative **22** was also investigated. Irradiation of each sample (ca. $10^{-5}$ M) was performed at intervals for at least 10 min in total, and the absorbance maximum of the corresponding VHF species was plotted against the time of irradiation. By curve fitting, the time at which half of the DHA had been converted into VHF was determined. After correcting for different concentrations and differences in sample absorbances (for details, see Supporting Information), we obtain the following estimated ratios of "quantum yields" for the ring-opening reaction, $\phi$ (compound)/$\phi$ (**1**) = 0.03 (**3b**), 0.04 (**3a**), 0.2 (**4**), 0.3 (**6**), 0.7 (**5**), 1.0 (**1** + $C_{60}$, 1:1) (Figure 3). When performing the light-induced ring-opening on **3a** and **5** at about 10 times more dilute concentrations, we obtain a similar ratio in quantum yields of ring-opening for the two species as that obtained at the higher concentration ($\phi$ (**5**)/$\phi$ (**3a**) ~17–19 from the two experiments). The ratios in quantum yields listed above present some rough estimates, but the data show a clear trend: the closer $C_{60}$ is placed to the DHA, the lower the ratio of quantum yields. In other words, a covalently attached $C_{60}$ exerts a quenching influence on the ring-opening, which is possibly explained by light-induced electron transfer to this acceptor unit (although we cannot exclude other quenching mecha-


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Table 1. Absorption Maxima of DHAs and VHFs (25 °C) and Measured Rate Constants for Thermally Induced Back Reaction (VHF → DHA) at 50 °C[a]

| | $\lambda_{DHA}$ [nm] | $\varepsilon$ [Lmol$^{-1}$ cm$^{-1}$] | $\lambda_{VHF}$ [nm] | $\varepsilon$ [Lmol$^{-1}$ cm$^{-1}$] | $k_{50\ °C}$ [s$^{-1}$] | $t_{1/2,\ 50\ °C}$ [min] |
|---|---|---|---|---|---|---|
| **1** | 352 | | 475 | | | |
| **3a** | 329/362 (sh) | 30/25 × 10$^3$ | 478 | 15 × 10$^3$ | 30.3 × 10$^{-5}$ | 38.1 |
| **3b** | 329/357 (sh) | 45/40 × 10$^3$ | 476 | 10 × 10$^3$ | 37.4 × 10$^{-5}$ | 30.9 |
| **4** | 313/372 (sh) | 56/45 × 10$^3$ | 480 | 25 × 10$^3$ | 70.6 × 10$^{-5}$ | 16.4 |
| **5** | 381 | 40 × 10$^3$ | 480 | 19 × 10$^3$ | 71.0 × 10$^{-5}$ | 16.3 |
| **6** | 381 | 29 × 10$^3$ | 481 | 14 × 10$^3$ | 81.1 × 10$^{-5}$ | 14.2 |
| **17** | 384 | 38 × 10$^3$ | 482 | 28 × 10$^3$ | 61.9 × 10$^{-5}$ | 18.7 |
| **18** | 386 | 36 × 10$^3$ | 480 | 18 × 10$^3$ | 73.2 × 10$^{-5}$ | 15.8 |

[a]Solvent: 1,2-dichloroethane; sh = shoulder.

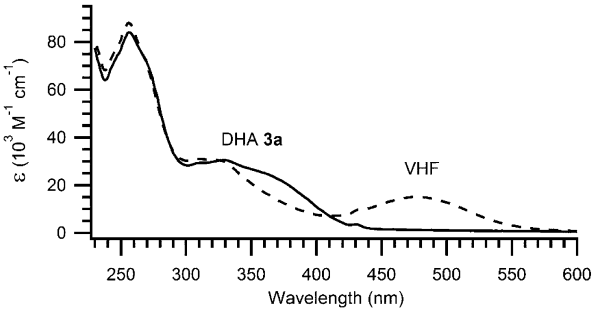


**Figure 2.** Absorption spectra of DHA **3a** and its corresponding VHF in 1,2-dichloroethane.

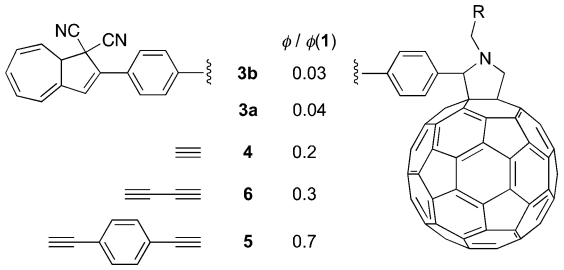


**Figure 3.** Structures of DHA-$C_{60}$ conjugates and estimated quantum yields ($\phi$) for the DHA → VHF conversion relative to that of DHA **1**, i.e., quantum yield ratios.

nisms). It is important to note that **3b** (devoid of a propyloxyphenol unit) undergoes the light-induced ring-opening reaction least readily, which signals that although the propyloxyphenol substituent may also play a role, the large effect originates from $C_{60}$. The strong dependence on the separation between DHA and $C_{60}$ seems to indicate that the quenching is of intramolecular origin. Nevertheless, the formation of a complex between DHA **2** and $C_{60}$ in the solid state prompted us to investigate the possibility of quenching by simply adding the $C_{60}$ derivative **22** to a solution of DHA **1**. However, addition of 1 equiv of **22** had no influence, supporting that any weak association between the two units in solution cannot account for the quenching observed in the conjugates. The quenching influence of an electron acceptor is in accordance with our previous studies on a DHA-TTF conjugate (TTF = tetrathiafulvalene).[25] Oxidation of the TTF unit to its corresponding radical cation (turning it into an acceptor unit) thus had a retarding influence on the ring-opening reaction.

## CONCLUSION

In conclusion, we have developed efficient synthetic protocols for linking together the dihydroazulene photoswitch to Buckminsterfullerene via conjugated phenyleneethynylene bridges. In one procedure, the products are obtained by a final Prato reaction. Useful dihydroazulene and $C_{60}$ building blocks for acetylenic scaffolding were developed and were successfully coupled together by Sonogashira, Hay, and Cadiot−Chodkiewicz reactions, providing convenient alternative ways of obtaining DHA-$C_{60}$ conjugates. These coupling reactions have previously been used only scarcely on $C_{60}$ derivatives, but as shown here they are indeed viable methods to pursue further in the future. The light-induced ring-opening reaction was found to depend strongly on the distance between the two units. Thus, the $C_{60}$ end group was observed to quench the ring-opening reaction. These results are important for the further exploration of the conjugates in light-controlled molecular electronics devices when using $C_{60}$ as an anchoring group. Our recently developed synthesis protocols[21,24] for functionalizing the DHA core at the seven-membered ring may allow incorporation of fullerene anchoring groups at both poles of the molecule via linkers of suitable lengths. It would be particularly interesting to investigate the conductivity of such dumbbell-like molecules in single-molecule junctions and, in particular, the possibility for light-induced conductance switching.

## EXPERIMENTAL SECTION

**General Methods.** Chemicals were used as purchased from commercial sources. THF was distilled from sodium/benzophenone couple. Compounds **2**,[7] **7**,[17] **16**,[10g] and **26**[23] were synthesized according to the respective literature procedures. Purification of products was carried out either by flash chromatography on silica gel (40−63 $\mu$m) or by dry column vacuum chromatography (DCVC)[26] (15−40 $\mu$m). Thin-layer chromatography (TLC) was carried out using aluminum sheets precoated with silica gel. $^1$H NMR (500 MHz) and $^{13}$C NMR (125 MHz) spectra were recorded on an instrument with cryoprobe using the residual solvent as the internal standard ($CDCl_3$, $^1$H 7.26 ppm and $^{13}$C 77.16 ppm; $CD_3OD$, $^1$H 4.87 ppm and $^{13}$C 49.00 ppm.) All chemical shifts are quoted on the $\delta$ scale (ppm), and all coupling constants ($J$) are expressed in Hz. In APT spectra (Supporting Information), CH and $CH_3$ correspond to negative signals and C and $CH_2$ correspond to positive signals. Matrix assisted laser desorption ionization (MALDI) mass spectra were recorded on a time-of-flight apparatus; all measurements were performed in negative ion mode with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. Neat IR spectra were acquired using an 'ATR platinum Diamond 1 Refl' accessory or as films upon a silicon window. Melting points are uncorrected. UV−vis spectroscopic measurements were performed in a 1-cm path length quartz cuvette.


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**Ethyl-2-(4-propyloxybenzylamino)acetate (8).** To a solution of 4-propyloxybenzaldehyde **7** (6.20 g, 37.8 mmol), glycine ethylester hydrochloride (5.05 g, 36.3 mmol), and $NEt_3$ (5.8 mL, 40 mmol) in dry $CH_2Cl_2$ (50 mL) was added 3 Å molecular sieves. The mixture was allowed to stir at rt for 16 h. The resulting mixture was filtered, and the solvent was removed under reduced pressure to give the imine as a white solid. The solid was then dissolved in MeOH (50 mL), and the mixture was cooled by an ice bath. Sodium borohydride (1.55 g, 40.8 mmol) was carefully added portion-wise to the stirring solution. After 10 min, saturated aqueous sodium bicarbonate (100 mL) was added, and the reaction mixture was extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic phases were dried over $Na_2SO_4$ and filtered, and the solvent was removed to give a crude oil, which was subsequently purified by column chromatography ($SiO_2$, 3:2 EtOAc/heptane) to give the title compound as a colorless oil (6.52 g, 69%). $R_f$ = 0.34 (3:2 EtOAc/heptane). IR (ATR) $\nu_{max}$ ($cm^{-1}$): 3341w, 3063w, 3032w, 2956m, 2937m, 2876m, 1736vs, 1652m, 1611s, 1583m, 1510vs, 1465s, 1420m, 1392s, 1376sh. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.24−7.21 (m, 2H), 6.86−6.84 (m, 2H), 4.18 (q, $J$ = 7.1 Hz, 2H), 3.90 (t, $J$ = 6.6 Hz, 2H), 3.73 (s, 2H), 3.38 (s, 2H), 1.87 (broad s, 1H), 1.83−1.76 (m, 2H), 1.27 (t, $J$ = 7.1 Hz, 3H), 1.03 (t, $J$ = 7.4 Hz, 3H). $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ 172.6, 158.5, 131.5, 129.6, 114.6, 69.6, 60.8, 52.8, 50.1, 22.7, 14.4, 10.6. ES-MS: $m/z$ 274 ($[M + Na]^+$), 252 ($[M + H]^+$). Anal. Calcd for $C_{14}H_{21}NO_3$: C 66.91, H 8.42, N 5.57. Found: C 67.08, H 8.49, N 5.47.

**2-(4-Propyloxybenzylamino)acetic Acid (9).** To a solution of **8** (5.47 g, 21.8 mmol) in 50% aqueous MeOH (100 mL) was added NaOH (1.42 g, 35.5 mmol), and the mixture was stirred until TLC indicated complete consumption of the starting material. The MeOH was removed by rotary evaporation, and the solution was diluted further with water (100 mL). The solution was acidified with aqueous 1 M HCl until pH 6.7 was achieved. The white precipitate was filtered and washed with water several times to afford the title amino acid as white solid (3.46 g, 71%). The amino acid was dried under high vacuum for 24 h prior to use in subsequent Prato reactions. Mp 197.5−198.5 °C. IR (ATR) $\nu_{max}$ ($cm^{-1}$): 3011m, 2967m, 2937m, 2917m, 2873m, 2790m, 2697m, 3200−2700brm, 2700−2000brm, 1908brw, 1597vs, 1514s, 1463s, 1451s, 1430s, 1395vs. $^1H$ NMR (500 MHz, $CD_3OD$): $\delta$ 7.39−7.36 (m, 2H), 6.98−6.95 (m, 2H), 4.11 (s, 2H), 3.95 (t, $J$ = 6.6 Hz, 2H), 3.44 (s, 2H), 1.83−1.76 (m, 2H), 1.04 (t, $J$ = 7.4 Hz, 3H). The amine NH and acid $CO_2H$ protons were not visible due to exchange. $^{13}C$ NMR (125 MHz, $CD_3OD$): $\delta$ 170.8, 161.5, 132.4, 124.6, 116.0, 70.7, 51.5, 23.6, 10.8. ES-MS: $m/z$ 246 ($[M + Na]^+$), 224 ($[M + H]^+$). Anal. Calcd for $C_{12}H_{17}NO_3$: C 64.55, H 7.67, N 6.27. Found: C 64.76, H 7.67, N 6.18.

**Methyl 4-(1,1-Dicyanoprop-1-en-2-yl)benzoate (11).** HMDS (7.1 mL, 5.4 g, 34 mmol) was carefully added to AcOH (18.8 mL, 19.7 g, 328 mmol). Upon completion, a solution of malononitrile (3.71 g, 56.1 mmol) and **10** (5.00 g, 28.1 mmol) in AcOH (9.3 mL, 9.7 g, 162 mmol) was added, and the resulting reaction mixture was stirred for 48 h at 75 °C. The solution was poured into water (300 mL) and extracted with $Et_2O$ (3 × 100 mL). The combined extracts were washed with water (2 × 100 mL) and brine (100 mL), dried over $MgSO_4$, and filtered, and the solvents were evaporated under reduced pressure. The residue was triturated from EtOAc/heptanes to yield the product as a yellow solid (5.97 g, 94%). Mp 95.2−96.6 °C $R_f$ = 0.27 (3:7 EtOAc/heptanes). IR (ATR) $\nu_{max}$ ($cm^{-1}$): 3105vw, 3000vw, 2851w, 2226m, 1717s, 1608w, 1584m, 1557m, 1500w, 1434m, 1405m, 1381m, 1308m, 1279vs, 1183s. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 8.16 (d, $J$ = 8.7 Hz, 2H), 7.59 (d, $J$ = 8.7 Hz, 2H), 3.96 (s, 3H), 2.66 (s, 3H) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ 174.4, 165.9, 140.0, 133.4, 130.4, 127.5, 112.4, 86.4, 52.7, 24.4 ppm. Anal. Calcd for $C_{13}H_{10}N_2O_2$: C 69.00, H 4.46, N 12.39. Found: C 68.92, H 4.24, N 12.46. ES-MS: $m/z$ 249 ($[M + Na]^+$), 227 ($[M + H]^+$).

**Methyl 4-(1,1-Dicyano-1,8a-dihydroazulen-2-yl)benzoate (13).** To a solution of **11** (4.00 g, 17.7 mmol) in $CH_2Cl_2$ (250 mL) was added tropylium tetrafluoroborate (3.15 g, 17.7 mmol), and the vessel was cooled to −78 °C. $NEt_3$ (2.7 mL, 19.4 mmol) was added in portions of 0.1 mL over 10 min. The reaction mixture was stirred overnight during which the contents were allowed to reach rt. Due to the presence of starting material adjudged by TLC, the mixture was again cooled to −78 °C where additional tropylium tetrafluoroborate (1.28 g, 7.19 mmol) and $NEt_3$ (1.00 mL, 7.19 mmol) were added. The mixture was stirred for a further 4 h. The reaction mixture was poured into brine, the organic phase was separated and dried over $MgSO_4$ and filtered, and the solvents were removed in vacuo, yielding a yellow oil consisting of a mixture of **12a** and **12b** and a small amount of cycloheptatriene according to crude NMR. An aliquot of the mixture was purified by dry column vacuum chromatography ($SiO_2$, 12.6 $cm^2$, 0−40% EtOAc/heptanes, 4% steps, 40 mL fractions), and compound **12a** was isolated as a colorless oil. Due to the instability, the remains of the reaction mixture were used directly in the next step. Compound **12a**: $R_f$ = 0.37 (3:7 EtOAc/heptanes). IR (neat) $\nu_{max}$ ($cm^{-1}$): 3019s, 2953s, 2847m, 2253m, 2231s, 1717vs, 1662m, 1609m, 1583m, 1561 m. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 8.13 (d, $J$ = 8.6 Hz, 1H), 7.45 (d, $J$ = 8.6 Hz, 1H), 6.65 − 6.54 (m, 1H), 6.25 − 6.15 (m, 1H), 5.14 (dd, $J$ = 9.1, 6.4 Hz, 1H), 3.94 (s, 2H), 3.19 (d, $J$ = 8.0 Hz, 1H), 2.02−1.88 (m, 1H) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ 177.2, 165.9, 138.9, 133.1, 131.3, 130.4, 127.5, 126.7, 122.7, 112.1, 87.9, 52.7, 39.0, 37.6 ppm. ES-MS: $m/z$ 339 ($[M + Na]^+$). The oil was dissolved in 1,2-dichloroethane (250 mL). Tritylium tetrafluoroborate (5.84 g, 17.7 mmol) was added, and the resulting dark red solution was stirred for 2 h at 80 °C. The reaction mixture was cooled to 0 °C, after which $NEt_3$ (2.46 mL, 17.7 mmol) was added in portions over 1 h, and the mixture was allowed to heat to rt. The black reaction mixture was then heated to 80 °C for 1 h. After cooling, the solvents were removed in vacuo. Purification by flash column chromatography ($SiO_2$, 33% EtOAc/heptanes) followed by recrystallization from $CCl_4$ gave **13** (1.25 g, 22%) as a dark yellow crystalline solid. Mp 153.6−155.0 °C, lit.[19] 152 °C. $R_f$ = 0.52 (1:1 EtOAc/heptanes). IR (neat) $\nu_{max}$ ($cm^{-1}$): 3022w, 2952w, 2249w, 1722s, 1606m, 1586w, 1559w. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 8.14−8.12 (m, 2H), 7.82−7.79 (m, 2H), 7.00 (s, 1H), 6.60 (dd, $J$ = 11.2, 6.3 Hz, 1H), 6.52 (dd, $J$ = 11.2, 6.1 Hz, 1H), 6.41 (broad d, $J$ = 6.3 Hz, 1H), 6.32 (ddd, $J$ = 10.2, 6.1, 2.1 Hz, 1H), 5.83 (dd, $J$ = 10.2, 3.8 Hz, 1H), 3.95 (s, 3H), 3.84 (ddd, $J$ = 3.8, 2.1, 2.1 Hz, 1H) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ 166.3, 139.1, 138.4, 134.7, 134.5, 131.7, 131.2, 131.0, 130.6, 127.9, 126.3, 122.4, 119.7, 115.0, 112.6, 52.5, 51.2, 45.2 ppm. ES-MS: $m/z$ 337 ($[M + Na]^+$).

**2-(4-Formylphenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (14).** A solution of DIBAL-H (3.0 mL, 1M in heptane, 3.0 mmol) was added in portions over 6 h to a stirred solution of the ester **13** (296 mg, 0.94 mmol) in dry toluene (50 mL) at −89 °C. The reaction was quenched with aqueous 0.1 M HCl (50 mL), and extracted with $Et_2O$ (2 × 50 mL). The combined organic phases were washed with aqueous $NH_4Cl$ (3 × 50 mL) and concentrated in vacuo. Purification by flash column chromatography ($SiO_2$, 10% THF/heptane) gave the aldehyde **14** as a yellow solid (23 mg, 9%). Mp 151−152 °C. $R_f$ = 0.44 (1:1 EtOAc/heptanes). IR (neat) $\nu_{max}$ ($cm^{-1}$): 2956w, 2925w, 2853w, 2200w, 1700s, 1603m, 1581w, 1560w. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 10.06 (s, 1H), 8.00−7.97 (m, 2H), 7.91−7.89 (m, 2H), 7.04 (s, 1H), 6.60 (dd, $J$ = 11.2, 6.2 Hz, 1H), 6.54 (dd, $J$ = 11.2, 6.1 Hz, 1H), 6.44 (broad d, $J$ = 6.1 Hz, 1H), 6.34 (ddd, $J$ = 10.2, 6.2, 2.1 Hz, 1H), 5.85 (dd, $J$ = 10.3, 3.9 Hz, 1H), 3.83 (ddd, $J$ = 3.9, 2.1, 2.1 Hz, 1H). $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ 191.2, 138.7, 138.2, 136.8, 136.0, 135.2, 132.0, 130.9, 130.6, 128.0, 126.8, 122.9, 119.7, 114.9, 112.5, 51.2, 45.2. ES-MS: $m/z$ 307 ($[M + Na]^+$), 285 ($[M + H]^+$).

**DHA-$C_{60}$ Conjugate (3a).** A degassed mixture of $C_{60}$ (151 mg, 0.210 mmol), compound **14** (31 mg, 0.109 mmol), and 2-(4-propoxybenzylamino)acetic acid (**9**) (128 mg, 0.549 mmol) in toluene (100 mL) was refluxed for 12 h. The solvent was removed under reduced pressure, and the crude residue was subjected to column chromatography ($SiO_2$, gradient elution from $CS_2$ to 3:7 toluene/$CS_2$) to afford the title compound as a dark brown solid (22 mg, 17%). $R_f$ = 0.35 (3:7 toluene/$CS_2$). IR (ATR) $\nu_{max}$ ($cm^{-1}$): 3017vw, 2955w, 2914w, 2887w, 2785w, 1607m, 1580w, 1507s, 1461m, 1418m, 1374w, 1356w, 1298w, 1237s. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 8.05 (broad s, 2H), 7.83 (broad d, $J$ = 7.8 Hz, 2H), 7.57−7.53 (m, 2H), 7.04−7.01 (m, 2H), 6.92 and 6.91 (2*s*, 1H), 6.58−6.54 (m, 1H), 6.49−6.45 (m, 1H), 6.33 (broad d, $J$ = 6.0 Hz, 1H), 6.31−6.28 (m, 1H), 5.82−5.79 (m, 1H), 5.22 (s, 1H), 4.86 (d, $J$ = 9.5 Hz, 1H), 4.49 and 4.48 (2*d*, $J$ =


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13.2 Hz, 1H), 4.18 (d, $J$ = 9.5 Hz, 1H), 4.00 and 3.99 (2$d$, $J$ = 6.6 Hz, 2H), 3.79−3.76 (m, 1H), 3.67 (d, $J$ = 13.2 Hz, 1H), 1.89−1.82 (m, 2H), 1.07 and 1.08 (2$t$, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 158.9, 156.4, 156.4, 154.1, 153.2, 153.0, 153.0, 147.5, 146.7, 146.5, 146.5, 146.4, 146.4, 146.3, 146.3, 146.3, 146.1, 146.1, 146.1, 146.1, 145.9, 145.7, 145.7, 145.6, 145.6, 145.5, 145.5, 145.5, 145.5, 145.4, 145.34, 145.3, 144.9, 144.8, 144.8, 144.6, 144.5, 143.3, 143.1, 142.8, 142.7, 142.7, 142.7, 142.5, 142.4, 142.3, 142.3, 142.3, 142.3, 142.2, 142.1, 142.0, 141.8, 141.8, 141.7, 140.3, 140.3, 140.2, 140.1, 139.8, 139.8, 139.7, 139.6, 139.6, 138.7, 138.6, 137.2, 137.1, 136.6, 136.2, 135.8, 133.0, 133.0, 132.9, 131.1, 131.1, 131.0, 130.9, 130.3, 129.2, 129.2, 127.8, 127.8, 126.7, 126.7, 121.3, 121.3, 119.7, 119.5, 115.3, 115.2, 114.8, 112.8, 112.8, 80.9, 80.8, 80.8, 76.7, 69.7, 68.8, 68.8, 66.7, 56.3, 51.3, 51.3, 45.3, 45.3, 22.8, 10.8. MALDI-TOF-MS: $m/z$ 1165 ($M^-$). Anal. Calcd for $C_{90}H_{27}N_3O$: C 92.69, H 2.33, N 3.60. Found: C 92.54, H 2.30, N 3.58.

**DHA-$C_{60}$ Conjugate (3b).** A degassed mixture of $C_{60}$ (108 mg, 0.150 mmol), compound **14** (27 mg, 0.095 mmol), and *N*-ethylglycine (105 mg, 1.02 mmol) in toluene (70 mL) was refluxed for 16 h. The resulting brown solution was allowed to cool, and the solvent was removed in vacuo. The crude residue was purified by column chromatography ($SiO_2$, gradient elution from $CS_2$ to 1:4 toluene/$CS_2$) to give pure the title compound as a flaky brown solid (37 mg, 37%). $R_f$ = 0.40 (2:3 toluene/$CS_2$). IR (neat) $\nu_{max}$ ($cm^{-1}$): 3029w, 2970s, 2933s, 2250w, 1540m, 1509w, 1186s .$^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.93 (broad s, 2H), 7.79 (broad d, $J$ = 8.1 Hz, 2H), 6.90 (s, 1H), 6.58−6.54 (m, 1H), 6.49−6.45 (m, 1H), 6.33−6.28 (m, 2H), 5.82−5.79 (m, 1H), 5.14−5.12 (m, 2H), 4.18 (d, $J$ = 9.4 Hz, 1H), 3.79−3.76 (m, 1H), 3.36−3.29 (m, 1H), 2.69−2.62 (m, 1H), 1.56 − 1.49 (m, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 156.5, 156.5, 154.3, 153.3, 153.1, 153.0, 147.5, 147.5, 146.7, 146.6, 146.5, 146.4, 146.4, 146.3, 146.3, 146.3, 146.1, 146.1, 145. 9, 145.7, 145.7, 145.6, 145.5, 145.5, 145.4, 145.4, 145.3, 144.9, 144.8, 144.6, 143.3, 143.1, 142.9, 142.7, 142.7, 142.7, 142.5, 142.4, 142.3, 142.3, 142.3, 142.2, 142.1, 142.1, 142.0, 141.8, 141.7, 141.7, 140.4, 140.3, 140.2, 140.1, 139.9, 139.8, 139.8, 138.8, 138.7, 137.2, 137.2, 136.7, 136.1, 135.8, 132.9, 132.8, 131.1, 131.1, 131.0, 130.7, 130.4, 130.4, 130.4, 127.8, 127.8, 126.6, 121.2, 121.2, 119.6, 119.5, 115.3, 115.2, 112.8, 112.8, 81.9, 81.9, 76.7, 69.1, 66.6, 51.3, 51.3, 47.4, 13.5. Anal. Calcd for $C_{82}H_{19}N_3$: C 94.15, H 1.83, N 4.02. Found: C 94.02, H 1.77, N 3.98.

**2-{4-[2-(4-Formylphenyl)ethynyl]phenyl}-1,8a-dihydroazulene-1,1-dicarbonitrile (17).** To a degassed stirring solution of compound **2** (352 mg, 0.92 mmol) and 4-ethynylbenzaldehyde (**15**) (175 mg, 1.35 mmol) in a solvent mixture of THF (20 mL) and diisopropylamine (20 mL) were added sequentially CuI (21 mg, 0.11 mmol) and $Pd(PPh_3)_4$ (75 mg, 0.065 mmol). The mixture was stirred in the dark for 1 h. The solvent was removed in vacuo, and the crude material was purified by flash column chromatography ($SiO_2$, gradient elution from toluene to 1:19 EtOAc/toluene) and chromatographed a second time ($SiO_2$, $CH_2Cl_2$) to afford the title compound as a bright yellow solid (265 mg, 75%). Mp 185−187 °C (decomp). $R_f$ = 0.34 (3:7 THF/heptane). IR (ATR) $\nu_{max}$ ($cm^{-1}$): 3028w, 2834w, 2737w, 2244vw, 2211w, 2151vw, 1686s, 1594s, 1558m, 1515m, 1436w, 1411m, 1388m, 1363w. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 10.04 (s, 1H), 7.90−7.88 (m, 2H), 7.76−7.74 (m, 2H), 7.71−7.69 (m, 2H), 7.65−7.63 (m, 2H), 6.94 (s, 1H), 6.59 (dd, $J$ = 11.4, 5.9 Hz, 1H), 6.50 (dd, $J$ = 11.4, 6.1 Hz, 1H). 6.39 (broad d, $J$ = 5.9 Hz, 1H), 6.33 (ddd, $J$ = 10.2, 6.1, 2.1 Hz, 1H), 5.83 (dd, $J$ = 10.2, 3.8 Hz, 1H), 3.81 (ddd, $J$ = 3.8, 2.1, 2.1 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 191.5, 139.3, 138.6, 135.8, 133.4, 132.7, 132.4, 131.5, 131.0, 130.8, 129.8, 129.2, 127.9, 126.3, 124.3, 121.8, 119.6, 115.1, 112.7, 92.7, 91.2, 51.3 (doublet signal due to incomplete decoupling), 45.17. MALDI-TOF-MS: $m/z$ 384 ($M^-$). Anal. Calcd for $C_{27}H_{16}N_2O$: C 84.36, H 4.20, N 7.29. Found: C 84.44, H 4.31, N 7.33.

**2-{4-[2-(4-(2-(4-Formylphenyl)ethynyl)phenyl)ethynyl]-phenyl}-1,8a-dihydroazulene-1,1-dicarbonitrile (18).** To a degassed stirring solution of compound **2** (205 mg, 0.54 mmol) and 4-[(4-ethynylphenyl)ethynyl]benzaldehyde (**16**) (173 mg, 0.75 mmol) in a solvent mixture of THF (15 mL) and diisopropylamine (10 mL) were added sequentially CuI (10 mg, 0.053 mmol) and $Pd(PPh_3)_4$ (33 mg, 0.029 mmol). The resulting mixture was stirred in the dark for 2 h. The solvent was removed under reduced pressure, and the crude material was purified by flash column chromatography ($SiO_2$, gradient elution from toluene to 1:19 EtOAc/toluene) and chromatographed a second time ($SiO_2$, $CH_2Cl_2$) to give the product (156 mg, 60%) as a bright yellow solid. Mp 215−225 °C (decomp). $R_f$ = 0.35 (3:7 THF/heptane). IR (ATR) $\nu_{max}$ ($cm^{-1}$): 3043w, 3001vw, 2829w, 2730w, 2205w, 2158vw, 1701s, 1598m, 1579sh, 1559w, 1513m, 1431w, 1408m, 1381w. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 10.03 (s, 1H), 7.89−7.87 (m, 2H), 7.75−7.72 (m, 2H), 7.70−7.68 (m, 2H), 7.64−7.61 (m, 2H), 7.56 (s, 4H), 6.93 (s, 1H), 6.59 (dd, $J$ = 11.3, 6.2 Hz, 1H), 6.50 (dd, $J$ = 11.3, 6.0 Hz, 1H), 6.38 (broad d, $J$ = 6.2 Hz, 1H), 6.32 (ddd, $J$ = 10.2, 6.0, 2.1 Hz, 1H), 5.83 (dd, $J$ = 10.2, 3.9 Hz, 1H), 3.81 (ddd, $J$ = 3.9, 2.1, 2.1 Hz, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 191.5, 139.4, 138.6, 135.7, 133.2, 132.5, 132.3, 131.9, 131.9, 131.4, 131.0, 130.5, 129.4, 127.9, 126.3, 124.7, 123.6, 122.8, 121.7, 119.6, 115.1, 112.7, 93.1, 91.8, 91.2, 90.7, 51.3 (doublet due to incomplete decoupling), 45.2. MALDI-TOF-MS: $m/z$ 484 ($M^-$). Anal. Calcd for $C_{35}H_{20}N_2O$: C 86.76, H 4.16, N 5.78. Found: C 86.81, H 4.12, N 5.84.

**DHA-$C_{60}$ Conjugate (4).** *Method 1, Prato reaction.* A degassed mixture of $C_{60}$ (313 mg, 0.434 mmol), compound **17** (62 mg, 0.161 mmol), and 2-(4-propyloxybenzyl amino)acetic acid (**9**) (212 mg, 0.910 mmol) in toluene (150 mL) was heated to reflux for 12 h. The solvent was removed in vacuo, and the crude residue was subjected to column chromatography ($SiO_2$, gradient elution from $CS_2$ to 3:7 toluene/$CS_2$) to afford the title compound as a dark brown solid (93 mg, 46%). $R_f$ = 0.36 (3:7 toluene/$CS_2$). *Method 2, Sonogashira cross-coupling reaction.* A degassed solution of dry $NEt_3$ (2 mL) in toluene (10 mL) was added via cannula to fulleropyrrolidine aryl-iodide (**21**) (13.4 mg, 0.012 mmol), $Pd(PPh_3)_4$ (1.4 mg, 0.001 mmol), CuI (0.3 mg, 0.001 mmol), and **25** (17 mg, 0.06 mmol). After 7 h of stirring at 90 °C, the solvent was removed under reduced pressure. The crude material was purified by column chromatography ($SiO_2$, gradient elution from $CS_2$ to $CH_2Cl_2$) to yield pure title compound as a dark brown solid (5.1 mg, 33%). IR (ATR) $\nu_{max}$ ($cm^{-1}$): 3017w, 2858w, 2914w, 2867w, 2779w, 1739m, 1602w, 1580w, 1540w, 1507s, 1460m, 1423m, 1409sh, 1372m, 1353 m. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.95 (broad s, 2H), 7.74−7.71 (m, 2H), 7.65 (broad d, $J$ = 8.1 Hz, 2H), 7.62−7.59 (m, 2H), 7.56−7.54 (m, 2H), 7.04−7.01 (m, 2H), 6.91 (s, 1H), 6.57 (dd, $J$ = 11.3, 5.9 Hz, 1H), 6.49 (dd, $J$ = 11.3, 6.1 Hz, 1H), 6.36 (broad d, $J$ = 5.9 Hz, 1H), 6.31 (ddd, $J$ = 10.2, 6.1, 2.1 Hz, 1H), 5.82 (dd, $J$ = 10.2, 3.8 Hz, 1H), 5.19 (s, 1H), 4.85 (d, $J$ = 9.5 Hz, 1H), 4.49 (d, $J$ = 13.2 Hz, 1H), 4.17 (d, $J$ = 9.5 Hz, 1H), 4.00 (t, $J$ = 6.6 Hz, 2H), 3.79 (ddd, $J$ = 3.8, 2.1, 2.1 Hz, 1H), 3.67 (d, $J$ = 13.2 Hz, 1H), 1.91−1.80 (m, 2H), 1.08 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 158.9, 156.4, 154.2, 153.3, 153.2, 147.5, 146.8, 146.5, 146.5, 146.4, 146.4, 146.3, 146.3, 146.3, 146.2, 146.1, 146.1, 145.9, 145.7, 145.7, 145.5, 145.4, 145.4, 145.3, 144.9, 144.8, 144.6, 144.5, 143.3, 143.1, 142.8, 142.7, 142.7, 142.7, 142.5, 142.4, 142.3, 142.3, 142.2, 142.2, 142.0, 142.0, 141.8, 141.7, 140.3, 140.3, 140.1, 139.7, 139.5, 138.6, 138.1, 137.1, 136.6, 136.1, 135.8, 133.0, 132.5, 132.3, 131.3, 131.0, 130.3, 130.2, 129.3, 127.9, 126.3, 125.0, 123.1, 121.6, 119.6, 115.1, 114.8, 112.7, 92.1, 89.6, 81.0, 76.7, 69.7, 68.8, 66.6, 56.2, 51.3, 51.2, 45.1, 22.8, 10.8. MALDI-TOF-MS: $m/z$ 1265 ($M^-$). Anal. Calcd for $C_{98}H_{31}N_3O$: C 92.95, H 2.47, N 3.32. Found: C 92.80, H 2.39, N 3.26.

**DHA-$C_{60}$ Conjugate (5).** A degassed mixture consisting of $C_{60}$ (278 mg, 0.386 mmol), compound **18** (81 mg, 0.167 mmol), and 2-(4-propyloxybenzyl amino)acetic acid (**9**) (353 mg, 1.52 mmol) in toluene (150 mL) was heated to reflux for 12 h. The solvent was removed in vacuo, and the crude residue was subjected to column chromatography ($SiO_2$, gradient elution from $CS_2$ to 3:7 toluene/$CS_2$) to afford the title compound as a dark brown solid (102 mg, 45%). $R_f$ = 0.38 (3:7 toluene/$CS_2$). IR (ATR) $\nu_{max}$ ($cm^{-1}$): 3019w, 2962w, 2913w, 2868w, 2778w, 1602m, 1581sh, 1507s, 1461m, 1423m, 1409m, 1372m, 1352w. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.94 (broad s, 2H), 7.74−7.71 (m, 2H), 7.65 (broad d, $J$ = 8.1 Hz, 2H), 7.62−7.59 (m, 2H), 7.56−7.50 (m, 6H), 7.04−7.01 (m, 2H), 6.92 (s, 1H), 6.58 (dd, $J$ = 11.2, 5.9 Hz, 1H), 6.49 (dd, $J$ = 11.2, 6.1 Hz, 1H), 6.37 (broad d, $J$ = 5.9 Hz, 1H), 6.32 (ddd, $J$ = 10.2, 6.1, 2.1 Hz, 1H), 5.83 (dd, $J$ = 10.2,


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3.8 Hz, 1H), 5.18 (s, 1H), 4.85 (d, $J$ = 9.5 Hz, 1H), 4.49 (d, $J$ = 13.2 Hz, 1H), 4.17 (d, $J$ = 9.5 Hz, 1H), 4.00 (t, $J$ = 6.6 Hz, 2H), 3.80 (ddd, $J$ = 3.8, 2.1, 2.1 Hz, 1H), 3.67 (d, $J$ = 13.2 Hz, 1H), 1.90−1.82 (m, 2H), 1.08 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 158.9, 156.5, 154.2, 153.3, 153.2, 147.5, 147.5, 146.8, 146.5, 146.5, 146.4, 146.4, 146.3, 146.3, 146.3, 146.2, 146.1, 146.1, 145.9, 145.7, 145.7, 145.5, 145.5, 145.4, 145.4, 145.3, 144.9, 144.8, 144.6, 144.5, 143.3, 143.1, 142.8, 142.7, 142.7, 142.7, 142.5, 142.4, 142.3, 142.3, 142.2, 142.2, 142.2, 142.0, 142.0, 141.8, 141.7, 140.3, 140.3, 140.1, 139.7, 139.5, 138.6, 137.1, 136.6, 136.1, 135.8, 133.1, 132.5, 131.8, 131.7, 131.3, 131.0, 130.3, 130.3, 129.3, 127.9, 126.3, 124.9, 123.5, 123.3, 122.9, 121.6, 119.6, 115.1, 114.8, 112.7, 92.0, 91.4, 90.8, 90.0, 81.0, 81.0, 76.8, 69.7, 68.8, 66.6, 56.2, 51.3, 51.2, 45.2, 22.8, 10.8. MALDI-TOF-MS: $m/z$ 1365 ($M^-$). Anal. Calcd for $C_{106}H_{35}N_3O$: C 93.17, H 2.58, N 3.08. Found: C 93.09, H 2.68, N 3.01.

**Fulleropyrrolidine Aryl-iodide (21).** To a degassed solution of $C_{60}$ (200 mg, 0.28 mmol) in dry toluene (150 mL) were added 2-(4-propoxybenzylamino)acetic acid (**9**) (375 mg, 1.62 mmol) and 4-iodobenzaldehyde (**19**) (78 mg, 0.34 mmol). The contents of the reaction vessel were refluxed for 2 h. The solvent was removed in vacuo, and the crude residue was purified by column chromatography ($SiO_2$, gradient elution from $CS_2$ to 1:4 toluene/$CS_2$) to yield the title compound **21** as a dark brown solid (122 mg, 39%). $R_f$ = 0.33 (1:19 toluene/$CS_2$). IR (ATR) $\nu_{max}$ ($cm^{-1}$): 2954w, 2912w, 2868w, 2779w, 1606m, 1580m, 1507vs, 1479s, 1461s, 1423s, 1402m, 1371m, 1352m, 1333m, 1231vs, 1165vs. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.82 (broad d, $J$ = 7.9 Hz, 2H), 7.70 (broad s, 2H), 7.58−7.50 (m, 2H), 7.07−6.99 (m, 2H), 5.13 (s, 1H), 4.86 (d, $J$ = 9.6 Hz, 1H), 4.46 (d, $J$ = 13.2 Hz, 1H), 4.17 (d, $J$ = 9.6 Hz, 1H), 4.02 (t, $J$ = 6.5 Hz, 2H), 3.66 (d, $J$ = 13.2 Hz, 1H), 1.92−1.85 (m, 2H), 1.10 (t, $J$ = 7.4 Hz, 3H).$^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 158.8, 156.4, 154.1, 153.2, 153.1, 147.5, 147.4, 146.7, 146.5, 146.4, 146.3, 146.3, 146.3, 146.2, 146.1, 146.1, 146.1, 145.8, 145.7, 145.6, 145.6, 145.5, 145.5, 145.4, 145.4, 145.3, 144.8, 144.7, 144.5, 144.5, 143.3, 143.1, 142.8, 142.7, 142.7, 142.5, 142.3, 142.3, 142.2, 142.1, 142.1, 142.0, 141.8, 141.7, 140.3, 140.3, 140.1, 139.7, 138.1, 137.1, 137.1, 136.5, 136.1, 135.8, 131.5, 130.2, 129.2, 114.8, 94.5, 80.7, 76.5, 69.7, 68.7, 66.6, 56.2, 22.8, 10.8. MALDI-TOF-MS: $m/z$ 1113 ($M^-$). Anal. Calcd for $C_{78}H_{20}NIO$: C 84.09, H 1.81, N 1.26. Found: C 84.19, H 1.73, N 1.35.

**Fulleropyrrolidine Aryl-ethynyl (22).** To a degassed solution of $C_{60}$ (200 mg, 0.28 mmol) in dry toluene (150 mL) were added 2-(4-propoxybenzylamino)acetic acid (**9**) (375 mg, 1.62 mmol) and 4-ethynylbenzaldehyde (**20**) (72 mg, 0.56 mmol). The resulting mixture was refluxed for 4 h. The solvent was removed in vacuo, and the crude material was purified by column chromatography ($SiO_2$, gradient elution from $CS_2$ to 1:4 toluene/$CS_2$) to give the title compound as a brown solid (147 mg, 53%). $R_f$ = 0.30 (1:19 toluene/$CS_2$). IR (ATR) $\nu_{max}$ ($cm^{-1}$): 3288w, 2913w, 2868w, 2774w, 2194vw, 1672w, 1605w, 1573w, 1506s, 1461m, 1422m, 1371w, 1333w, 1296w, 1224s, 1168s. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.90 (broad s, 2H), 7.60 (broad d, $J$ = 8.2 Hz, 2H), 7.54−7.51 (m, 2H), 7.04−6.98 (m, 2H), 5.16 (s, 1H), 4.84 (d, $J$ = 9.5 Hz, 1H), 4.46 (d, $J$ = 13.2 Hz, 1H), 4.16 (d, $J$ = 9.5 Hz, 1H), 3.99 (t, $J$ = 6.6 Hz, 2H), 3.65 (d, $J$ = 13.2 Hz, 1H), 3.10 (s, 1H), 1.89−1.82 (m, 2H), 1.08 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 158.9, 156.4, 154.2, 153.2, 153.1, 147.5, 147.5, 146.8, 146.5, 146.4, 146.4, 146.4, 146.3, 146.3, 146.3, 146.1, 146.1, 146.1, 145.9, 145.7, 145.7, 145.6, 145.6, 145.5, 145.5, 145. 5, 145.4, 145.4, 145.3, 144.9, 144.8, 144.6, 144.5, 143.3, 143.1, 142.8, 142.7, 142.7, 142.7, 142.5, 142.4, 142.3, 142.3, 142.2 142.1, 142.0, 142.0, 141.8, 141.7, 140.3, 140.3, 140.0, 139.7, 138.2, 137.1, 136.6, 136.1, 135.8, 132.7, 130.3, 122.4, 114.7, 83.5, 80.9, 78.0, 76.7, 69.7, 68.8, 66.6, 56.2, 22.8, 10.8. MALDI-TOF-MS: $m/z$ 1011 ($M^-$). Anal. Calcd for $C_{80}H_{21}NO$: C 94.94, H 2.09, N 1.38. Found: C 94.80, H 2.21, N 1.32.

**Fulleropyrrolidine Derivative (23).** To a mixture of compound **21** (8 mg, 0.007 mmol), $Pd(PPh_3)_4$ (1 mg, 0.0009 mmol), and CuI (0.1 mg, 0.0005 mmol) was added a degassed solution of trimethylsilylacetylene (0.1 mL) and $NEt_3$ (2 mL) in toluene (10 mL). The reaction contents were stirred for 6 h at 90 °C, after which time the solvent was removed under reduced pressure. The crude residue was subsequently purified by chromatography ($SiO_2$, gradient elution from $CS_2$ to 1:19 toluene/$CS_2$) to afford the title compound as a dark brown solid (2.2 mg, 29%). $R_f$ = 0.31 (1:19 toluene/$CS_2$). IR (ATR) $\nu_{max}$ ($cm^{-1}$): 3032vw, 2958w, 2932w, 2786w, 2152m, 1611w, 1583vw, 1537s, 1510m, 1464m, 1426m, 1371m, 1353m, 1333m, 1297m, 1246vs. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.88 (broad s, 2H), 7.57 (broad d, $J$ = 8.0 Hz, 4H), 7.53−7.50 (m, 2H), 7.04−6.98 (m, 2H), 5.14 (s, 1H), 4.83 (d, $J$ = 9.5 Hz, 1H), 4.44 (d, $J$ = 13.2 Hz, 1H), 4.16 (d, $J$ = 9.5 Hz, 1H), 3.99 (t, $J$ = 6.5 Hz, 2H), 3.65 (d, $J$ = 13.2 Hz, 2H), 1.89−1.82 (m, 2H), 1.08 (t, $J$ = 7.4 Hz, 3H), 0.24 (s, 9H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 158.8, 156.4, 154.2, 153.3, 153.2, 147.5, 146.8, 146.5, 146.4, 146.4, 146.4, 146.3, 146.3, 146.3, 146.2, 146.1, 146.1, 145.9, 145.7, 145.6, 145.5, 145.5, 145.4, 145.4, 145.4, 145.3, 144.9, 144.8, 144.5, 144.5, 143.3, 143.1, 142.8, 142.7, 142.7, 142.7, 142.5, 142.4, 142.3, 142.3, 142.2, 142.0, 142.0, 141.8, 141.7, 140.3, 140.2, 140.0, 139.7, 137.9, 137.1, 136.6, 136.1, 135.8, 132.6, 130.3, 123.3, 114.8, 95.2, 80.9, 76.7, 69.8, 68.8, 66.6, 56.1, 22.8, 10.8, 0.1. MALDI-TOF-MS: $m/z$ 1083 ($M^-$). Anal. Calcd for $C_{83}H_{29}NOSi$: C 91.95, H 2.70, N 1.29. Found: C 92.03, H 2.65, N 1.16.

**2-[4-(Triisopropylsilylethynyl)phenyl]-1,8a-dihydroazulene-1,1-dicarbonitrile (24).** To a mixture of compound **2** (200 mg, 0.52 mmol), $PdCl_2(PPh_3)_2$ (20 mg, 0.026 mmol), and CuI (10 mg, 0.053 mmol) was added a degassed solution of triisopropylsilylacetylene (0.24 mL, 1.05 mmol) in $(i\text{-Pr})_2NH$ (0.2 mL) and THF (10 mL), and the mixture was stirred in darkness for 3 h at rt. The solvent was removed under reduced pressure, the residue was extracted with minimal toluene and filtered through cotton wool, and the solvent was removed in vacuo. The crude residue was purified by dry column chromatography ($SiO_2$, 80 mL fractions, gradient elution starting with heptane and increasing the $CH_2Cl_2$ content by 3 mL per fraction). The first yellow band yielded the title compound **24** as a yellow crystalline solid (168 mg, 74%). $R_f$ = 0.53 (1:1 $CH_2Cl_2$/heptane). Mp 131.5−133.0 °C. IR (ATR) $\nu_{max}$ ($cm^{-1}$): 3020w, 2944s, 2892m, 2864s, 2240vw, 2156m, 1599m, 1505m, 1462s, 1411m, 1387m, 1366 m. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.69−7.66 (m, 2H), 7.57−7.55 (m, 2H), 6.89 (s, 1H), 6.57 (dd, $J$ = 11.3, 6.2 Hz, 1H), 6.48 (dd, $J$ = 11.3, 6.0 Hz, 1H), 6.36 (broad d, $J$ = 6.2 Hz, 1H), 6.31 (ddd, $J$ = 10.2, 6.0, 2.1 Hz, 1H), 5.82 (dd, $J$ = 10.1, 3.8 Hz, 1H), 3.79 (ddd, $J$ = 3.8, 2.1, 2.1 Hz, 1H), 1.21−1.03 (m, 21H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 139.5, 138.6, 133.0, 132.9, 131.2, 131.0, 130.2, 127.8, 126.1, 125.3, 121.5, 119.6, 115.1, 112.7, 106.3, 94.2, 51.2 (doublet signal due to incomplete decoupling), 45.2, 18.8, 11.4, 1C masked. ES-MS (MeOH): $m/z$ 437 ($[M + H]^+$). Anal. Calcd for $C_{29}H_{32}N_2Si$: C 79.77, H 7.39, N 6.42. Found: C 79.57, H 7.40, N 6.36.

**2-(4-Ethynylphenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (25).** *Method 1.* To a solution of **24** (289 mg, 0.663 mmol) in THF (30 mL) were added AcOH (0.38 mL 6.6 mmol) and a solution of $Bu_4NF$ (1.33 mL, 1.33 mmol, 1 M) in THF dropwise. The reaction mixture was refluxed for 16 h (resulting in a light yellow-brown color), after which it was diluted with $Et_2O$ (50 mL), washed with water (3 × 50 mL), dried with $Na_2SO_4$, filtered, and concentrated in vacuo. Purification by dry column vacuum chromatography ($SiO_2$, 12.6 $cm^2$, 0−70% toluene/heptanes, 5% steps, then 70−80% toluene/heptanes, 2.5% steps, 40 mL fractions) gave **25** (137 mg, 76%) as a yellow solid. *For the alternative methods described in Scheme 7, see the* Supporting Information. $R_f$ = 0.24 (50% toluene/heptanes); $R_f$ = 0.50 (80% toluene/heptanes); $R_f$ = 0.31 (1:1 $CH_2Cl_2$/heptane). Mp 143.0−143.5 °C. IR (ATR) $\nu_{max}$ ($cm^{-1}$): 3280s, 3016w, 2954sh, 2922m, 2851m, 2244w, 2202vw, 1725w, 1602w, 1579w, 1504m, 1462m, 1411m, 1382w. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.71−7.68 (m, 2H), 7.59−7.57 (m, 2H), 6.91 (s, 1H), 6.58 (dd, $J$ = 11.2, 6.3 Hz, 1H), 6.49 (dd, $J$ = 11.2, 6.1 Hz, 1H), 6.37 (broad d, $J$ = 6.3 Hz, 1H), 6.31 (ddd, $J$ = 10.2, 6.1, 2.1 Hz, 1H), 5.82 (dd, $J$ = 10.2, 3.8 Hz, 1H), 3.79 (ddd, $J$ = 3.8, 2.1, 2.1 Hz, 1H), 3.22 (s, C≡CH 1H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 139.3, 138.5, 133.3, 133.0, 131.4, 131.0, 130.8, 127.9, 126.2, 123.9, 121.8, 119.6, 115.1, 112.7, 83.0, 79.9 (doublet signal due to incomplete decoupling), 51.2 (doublet signal due to incomplete decoupling), 45.2, 1C masked. ES-MS: $m/z$ 303 ($[M + Na]^+$). Anal. Calcd for $C_{20}H_{12}N_2$: C 85.69, H 4.31, N 9.99. Found: C 85.60, H 4.15, N 9.90.


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**2-{1-[4-(Trimethylsilylethynyl)phenyl]ethylidene}-malononitrile (27).** A mixture consisting of 4-(trimethylsilyl)ethynyl acetophenone (**26**) (3.79 g, 17.5 mmol), malononitrile (3.45 g, 52.3 mmol), and ammonium acetate (4.52 g, 58.7 mmol) in toluene (150 mL) and AcOH (6 mL) was refluxed for 2 h. The vessel was allowed to cool to rt, and the upper phase was decanted and washed with water (2 × 200 mL). The organic phase was dried over $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography ($SiO_2$, 3:17 EtOAc/heptanes) to afford the title compound **27** as a white solid (4.16 g, 90%). Mp 71−72 °C. $R_f$ = 0.33 (3:17 EtOAc/heptanes). IR (ATR) $\nu_{max}$ ($cm^{-1}$): 2956w, 2901w, 2224m, 2159m, 1599m, 1576s, 1544m, 1499m, 1408m, 1373 m. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.58−7.54 (m, 2H), 7.53−7.48 (m, 2H), 2.62 (s, 3H), 0.26 (s, 9H). $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ 174.2, 135.5, 132.6, 127.6, 127.5, 112.8, 103.6, 98.8, 85.0, 24.2, 24.2, 24.2, 24.1, −0.08. ES-MS: $m/z$ 287 ($[M + Na]^+$). Anal. Calcd for $C_{16}H_{16}N_2Si$: C 72.68, H 6.10, N 10.60. Found: C 72.44, H 6.08, N 10.57.

**2-{(2-Cyclohepta-2,4,6-trienyl)-1-[4-(trimethylsilylethynyl)-phenyl]ethylidene}malononitrile (28).** To a rapidly stirring suspension of tropylium tetrafluoroborate (2.89 g, 16.3 mmol) and dicyano compound **27** (3.90 g, 14.8 mmol) in dry $CH_2Cl_2$ (100 mL) at −78 °C, under an argon atmosphere, was added $NEt_3$ (2.4 mL, 17.0 mmol) during the course of 1 h. The contents were allowed to stir a further 10 min and aqueous 2 M HCl (20 mL) was added to the cold vessel after which time the cold bath was removed and the vessel was allowed to reach rt. The organic phase was washed twice with water, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo. The crude residue was purified by column chromatography ($SiO_2$, 3:17 EtOAc/heptanes) to afford the title compound **28** (4.90 g, 85%) as a yellowish oil. $R_f$ = 0.38 (3:17 EtOAc/heptane). IR (neat) $\nu_{max}$ ($cm^{-1}$): 3021w, 2960m, 2900w, 2230m, 2160m, 1602m, 1577m, 1542w, 1499w. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.56−7.52 (m, 2H), 7.38−7.33 (m, 2H), 6.60−6.58 (m, 2H), 6.20−6.17 (m, 2H), 5.12 (dd, $J$ = 9.1, 6.4 Hz, 2H), 3.18 (d, $J$ = 8.0 Hz, 2H), 1.96−1.90 (m, 2H), 0.26 (s, 9H). $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ 177.2, 134.3, 132.7, 131.3, 127.4, 127.2, 126.6, 122.8, 112.5, 103.6, 98.5, 86.7, 38.9, 37.9, −0.08. ES-MS: $m/z$ 393 ($[M + K]^+$), 377 ($[M + Na]^+$). HR-MS (ES+): $m/z$ 377.1439 ($[M + Na]^+$); calcd for $C_{23}H_{22}N_2NaSi^+$ $m/z$ 377.1444.

**2-[4-(Trimethylsilylethynyl)phenyl)]-1,8a-dihydroazulene-1,1-dicarbonitrile (29).** A mixture of cycloheptatriene compound **28** (4.21 g, 11.9 mmol) and tritylium tetrafluoroborate (4.12 g, 12.5 mmol) in dry $CH_2Cl_2$ (200 mL) was allowed to stir at rt for 16 h. The vessel was cooled in an ice bath, and then the mixture was treated with $NEt_3$ (1.8 mL, 12.8 mmol) and allowed to reach rt. The solvent was removed in vacuo, and MeCN (50 mL) was added to the flask, which was maintained at 50 °C for 30 min. The solvent was removed under reduced pressure, and the crude residue was purified by column chromatography ($SiO_2$, 1:1 $CH_2Cl_2$/heptanes) to afford the title compound as a glassy yellow solid (2.02 g, 48%). $R_f$ = 0.36 (1:1 $CH_2Cl_2$/heptanes). Mp 59−62 °C. IR (ATR) $\nu_{max}$ ($cm^{-1}$): 3020w, 2958m, 2898w, 2249w, 2201w, 2155s, 1600w, 1584w, 1505s, 1409m, 1390sh. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.68−7.66 (m, 2H), 7.55−7.53 (m, 2H), 6.90 (s, 1H), 6.57 (dd, $J$ = 11.3, 6.2 Hz, 1H), 6.49 (dd, $J$ = 11.3, 6.1 Hz, 1H), 6.36 (broad d, $J$ = 6.2 Hz, 1H), 6.31 (ddd, $J$ = 10.2, 6.1, 2.1 Hz, 1H), 5.81 (dd, $J$ = 10.2, 3.8 Hz, 1H), 3.79 (ddd, $J$ = 3.8, 2.1, 2.1 Hz, 1H), 0.27 (s, 9H). $^{13}C$ NMR (126 MHz, $CDCl_3$): $\delta$ 139.5, 138.6, 133.1, 132.8, 131.3, 131.0, 130.4, 127.8, 126.1, 125.0, 121.6, 119.6, 115.1, 112.7, 104.3, 97.6, 51.3 (doublet signal due to incomplete decoupling), 45.2, 0.0. MALDI-TOF-MS: $m/z$ 352 ($M^-$). Anal. Calcd for $C_{23}H_{20}N_2Si$: C 78.38, H 5.72, N 7.95. Found: C 78.55, H 5.68, N 7.81.

**2-(4′-Bromoethynylphenyl)-1,8a-dihydroazulene-1,1-dicarbonitrile (31).** To a stirred solution of **25** (102 mg, 0.364 mmol) in acetone (30 mL) were added NBS (102 mg, 0.573 mmol) and $AgNO_3$ (19 mg, 0.11 mmol, 30 mol %), and the solution was stirred at rt for 20 min. The yellow reaction mixture became milky since a white-yellow precipitate was formed. Water (50 mL) was added, the mixture was extracted with $CH_2Cl_2$ (100 mL), and the extract was washed with water (3 × 50 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. The yellow solid was redissolved in $CCl_4$ (25 mL), washed with saturated aqueous $NaS_2O_3$ (10 mL) and saturated aqueous $NaHCO_3$ (3 × 20 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo, which gave **31** (121 mg, 92%) as an essentially pure yellow crystalline solid. $R_f$ = 0.58 (80% toluene/heptanes). $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.68 (d, $J$ = 8.7 Hz, 2H), 7.53 (d, $J$ = 8.7 Hz, 2H), 6.90 (s, 1H), 6.57 (dd, $J$ = 11.2, 6.3 Hz, 1H), 6.49 (dd, $J$ = 11.2, 6.1 Hz, 1H), 6.37 (broad d, $J$ = 6.3, Hz, 1H), 6.31 (ddd, $J$ = 10.2, 6.1, 2.1 Hz, 1H), 5.81 (broad d, $J$ = 10.2, 3.8 Hz, 1H), 3.79 (ddd, $J$ = 3.8, 2.1, 2.1 Hz, 1H) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ 139.3, 138.6, 133.3, 132.9, 131.4, 131.0, 130.6, 127.9, 126.2, 124.5, 121.8, 119.6, 115.1, 112.7, 79.6, 53.1, 51.2, 45.2. HR-MS (ESP+): $m/z$ 380.9990/382.9979 ($[M + Na]^+$) ($Br^{79/81}$); calcd for $C_{20}H_{11}Br^{79/81}N_2Na^+$: $m/z$ 380.9998/382.9978.

**DHA-$C_{60}$ Conjugate (6).** *Method 1.* To a solution of compounds **25** (72 mg, 0.26 mol) and **22** (76 mg, 0.075 mmol) in chlorobenzene (20 mL) were added CuCl (180 mg, 1.81 mmol) and TMEDA (0.5 mL) under an oxygen atmosphere, by the use of a balloon. The contents were stirred for 2 h at rt after which time the solution was passed through a short pad of silica gel. The solvent was removed, and the crude mixture was purified by column chromatography ($SiO_2$, gradient elution from $CS_2$ to 1:1 $CS_2$/toluene). The second component to elute from the column was identified as the title compound, which was isolated pure as a dark brown solid (25 mg, 26%). $R_f$ = 0.38 (2:3 toluene/$CS_2$). IR (ATR) $\nu_{max}$ ($cm^{-1}$): 3014vw, 2912w, 2867w, 2779w, 1603m, 1580m, 1507s, 1461m, 1424m, 1408m, 1373m, 1351m, 1333m, 1297m, 1224s, 1170s. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.93 (broad s, 2H), 7.71−7.69 (m, 2H), 7.64 (broad d, $J$ = 8.1 Hz, 2H), 7.61−7.58 (m, 2H), 7.55−7.52 (m, 2H), 7.04−7.01 (m, 2H), 6.92 (s, 1H), 6.58 (dd, $J$ = 11.3, 6.0 Hz, 1H), 6.50 (dd, $J$ = 11.3, 6.1 Hz, 1H), 6.37 (broad d, $J$ = 6.0 Hz, 1H), 6.31 (ddd, $J$ = 10.2, 6.1, 2.1 Hz, 1H), 5.82 (dd, $J$ = 10.2, 3.8 Hz, 1H), 5.18 (s, 1H), 4.84 (d, $J$ = 9.5 Hz, 1H), 4.46 (d, $J$ = 13.2 Hz, 1H), 4.16 (d, $J$ = 9.5 Hz, 1H), 4.00 (t, $J$ = 6.6 Hz, 2H), 3.79 (ddd, $J$ = 3.8, 2.1, 2.1 Hz, 1H), 3.66 (d, $J$ = 13.2 Hz, 1H), 1.90−1.81 (m, 2H), 1.08 (t, $J$ = 7.4 Hz, 3H). $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ 158.9, 156.4, 154.1, 153.1, 153.0, 147.5, 147.5, 146.7, 146.5, 146.5, 146.4, 146.4, 146.3, 146.3, 146.3, 146.1, 146.1, 146.0, 145.8, 145.7, 145.7, 145.6, 145.6, 145.5, 145.5, 145.4, 145.4, 145.3, 144.9, 144.8, 144.6, 144.5, 143.3, 143.1, 142.8, 142.7, 142.7, 142.7, 142.5, 142.4, 142.3, 142.3, 142.2, 142.1, 142.0, 141.8, 141.7, 140.3, 140.3, 140.0, 139.7, 139.2, 139.1, 138.5, 137.1, 136.5, 136.1, 135.8, 133.6, 133,4, 133.1, 131.5, 131.1, 131.0, 130.3, 127.9, 126.3, 123.5, 122.0, 121.9, 119.6, 115.0, 114.8, 112.6, 82.9, 81.2, 80.9, 80.9, 76.7, 76.7, 74.7, 69.7, 68.8, 66.6, 56.3, 51.2, 51.2, 45.1, 22.8, 10.8. MALDI-TOF-MS: $m/z$ 1289 ($M^-$). Anal. Calcd for $C_{100}H_{31}N_3O$: C 93.08, H 2.42, N 3.26. Found: C 92.89, H 2.33, N 3.17. *Method 2.* A degassed solution of $NEt_3$ (0.05 mL, mmol) in dry THF (15 mL) was added via cannula to a stirring mixture of **22** (56 mg, 0.055 mmol), **31** (20 mg, 0.056 mmol), $Pd(PPh_3)_4$ (4 mg, 0.0035 mmol), and CuI (1 mg, 0.005 mmol), and the resulting solution was heated by means of microwave to 70 °C for 10 h. The solvent was removed in vacuo, and the crude residue was purified by column chromatography ($SiO_2$, gradient elution 10% toluene/$CS_2$ to 40% toluene/$CS_2$) to afford the product **6** as a dark brown powder (27 mg, 38%).

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Different experimental procedures for synthesis of **25**, X-ray crystal structure of compound **17**, and further details on the complex between DHA **2** and $C_{60}$, photolysis and thermal switching studies, UV−vis absorption and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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## Notes

The authors declare no competing financial interest.

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