Synthesis of Isoxazolo[60]fullerenes with Dumb-Bell-Type Structure and Atropisomeric Properties

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New dumb-bell-type fullerene adducts **2**, **4**, and **8a–b** could be synthesized via bifunctional nitrile oxides. The [60]fullerene derivative **16** of this type was synthesized by twofold esterification with an isoxazolo[60]fullerene-carboxylic acid derivative. In the latter case the reaction was used to link the archimedic polyhedron fullerene with the platonic element cubane. When a bulky spacer between the fullerene units was used, atropisomeres **8a–b** occurred. The fullerene derivative **11** with an anthracene moiety exhibited axial chirality.

Introduction

The cycloaddition of nitrile oxides to C_{60} is a well-known reaction and a wide range of monoadducts have been synthesized over the past five years.[1][2] We have introduced the twofold cycloaddition of a bifunctional nitrile oxide to C_{60} to build a dumb-bell-type molecule.[3] Several examples of this dumb-bell-type compounds are reported in the literature utilizing different bifunctional reagents such as diazo compounds,[4] dienes,[5] and azomethinylides.[6] Recently we developed a method to open the heterocycle in the C-3′-unsubstituted isoxazolofullerene. With the obtained fullerenol a fullerenyl ester could be prepared in nearly quantitative yield.[7]

Our efforts in modifying nitrile oxide cycloadducts by hydrolysis of a C-3′-carboxylic ester of an isoxazolofullerene have proved successful. By esterification of the acid product, we synthesized a new dumb-bell fullerene derivative. Interesting stereochemical properties were found in atropisomeric compounds synthesized by cycloaddition reactions of C_{60} with nitrile oxides substituted by anthracene derivatives.

Results and Discussion

The dumb-bell-shaped compounds **2**, **4**, and **8a−b** could be prepared by addition of bifunctional nitrile oxides to C_{60} in toluene. In order to synthesize the fullerene derivatives **2** and **4**, the nitrile oxides, which are 1,3-dipoles, were generated in situ from the corresponding bis(chlorooximino) compounds by elimination of hydrogen chloride.

The precursors **1**[8] and **3**[9] were prepared according to literature procedures. Starting from the twofold amino acid ester **3**, the intermediate bis(chlorooximino) compound was generated and directly converted into the dinitrile dioxide derivative, which yielded the twofold monoadduct **4** by cycloaddition reaction with C_{60} (Scheme 1). Obviously the mono(chlorooximino) derivative was produced by substitution of one diazonium group by a chloride ion, which is consistent with the proposed mechanism of this reaction.[10] As a result, the fullerene derivative **5** could be isolated as a byproduct. Compound **2**, **4**, and **5** have been characterized by MALDI-TOF mass spectra, NMR, IR, and UV spectra. The number of signals in the ^{1}H- and ^{13}C-NMR spectra are reduced according to molecular mirror symmetry.

Oxidation of the dioxime **6** led to the light- and air-sensitive dinitrile dioxide **7**, which could be isolated in small quantities. Both compounds were characterized by NMR, IR and HRMS analysis. Cycloaddition of compound **7** to C_{60} resulted in two products **8a−b**, which we concluded to be atropic isomers (Scheme 2).

Anthracenediyl compounds **8a** and **8b** could be isolated. HPLC separation of the mixture led to a ratio of 9:1. The MALDI-TOF mass spectrum of each of these isomers showed a molecular peak at m/z = 1821 and an identical fraction pattern. An ion peak at m/z = 1101 was due to the loss of one C_{60}. The ^{1}H-NMR spectra for the two compounds were very similar. The minor fraction was too insoluble to record a ^{13}C-NMR spectrum, but the spectrum of the major fraction was consistent with either of the proposed dumb-bell shapes of the molecules. Evidence of steric hindrance could also be provided by synthesis of compounds **11**. Conversion of aldehyde **9** to the oxime **10** proceeded in good yield. Transformation of **10** to the intermediate nitrile oxide and direct linkage to C_{60} led to racemic **11**. The recorded ^{13}C-NMR spectrum indicated the absence of a mirror plane since all 60 carbon atoms of the fullerene group were detected. This confirmed that free rotation of the anthryl group around the fullerene unit is re-

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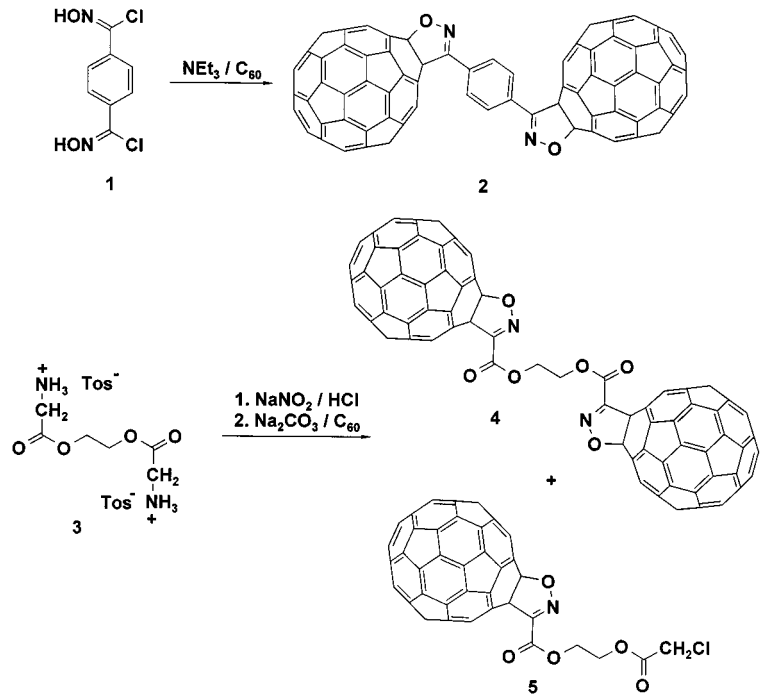
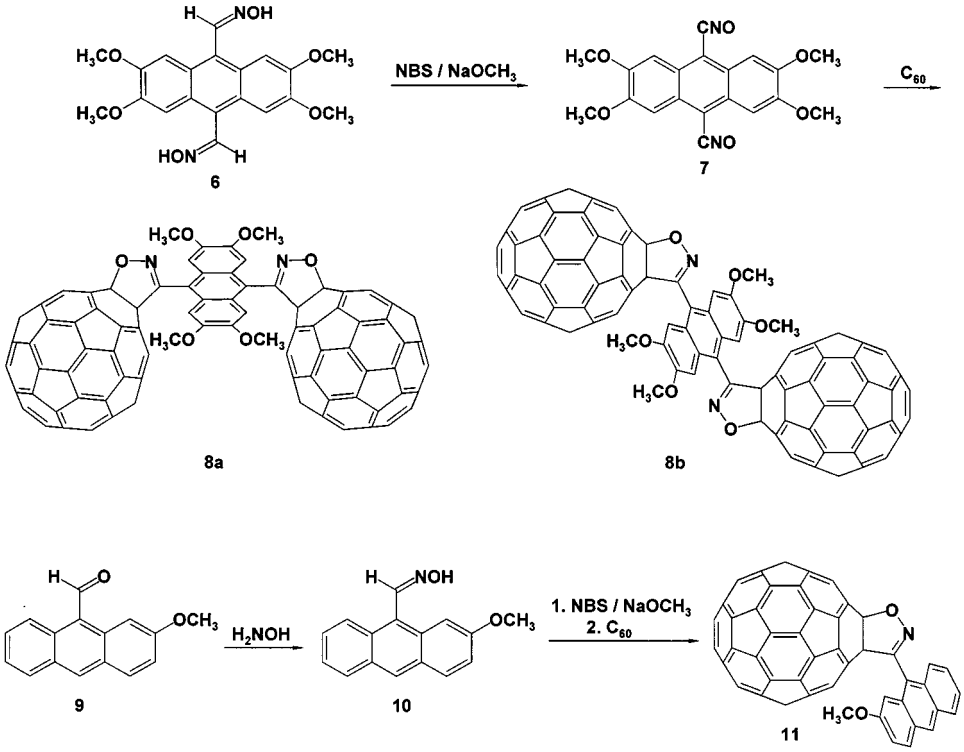


Scheme 1. Synthesis of the dumb-bell-type fullerenes

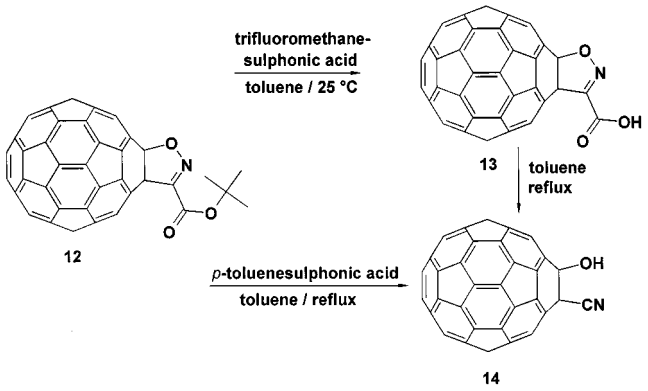


Scheme 2. Synthesis of the atropisomers **8a** and **8b** and the racemic **11** with axial chirality

stricted. Restricted rotations were also reported for other fullerene derivatives.[11]

The acid **13** was easily synthesized by hydrolysis of the corresponding *tert*-butyl ester **12**[2b] with trifluoromethanesulfonic acid at room temperature (Scheme 3).

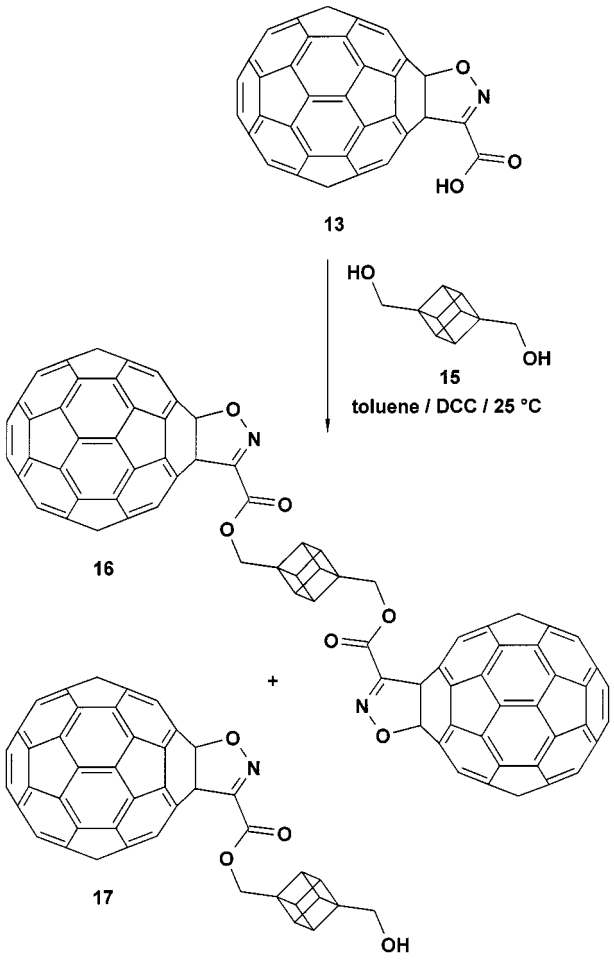
Once precipitated from toluene, the acid was highly insoluble, preventing full characterization. In the MALDI-TOF spectrum, the molecular ion peak and the $M^- - COOH$ peak could be found. A solid-state ^{13}C-NMR analysis under CPMAS conditions exhibited the signals of the car-



Scheme 3. Synthesis of the cyanofullerenol **14** by decarboxylation and ring opening of **13**

boxylic group (δ = 168.4) and the C(sp^3) atoms (δ = 108.1 and 75.3) in the expected regions. The peaks of the C(sp^2) atoms appeared as broad signals between δ = 140 and 150 also as expected. If the *tert*-butyl ester **12** was treated with *p*-toluenesulfonic acid at reflux in toluene, decarboxylation of the intermediate acid **13** occurred, yielding 24% of the fullerenol **14** (based on employed ester **12**) by ring opening. Fullerenol **14** can also be prepared by refluxing a solution of acid **13** in toluene. This type of reaction is known for the C-3 carboxylic acids of isoxazolines.[12] As we reported,[7] compound **14** was also synthesized by ring opening of the heterocycle in the C-3′-unsubstituted isoxazolofullerene but with a low yield of 5%. The yield can be increased to 71% if sodium methoxide is used as a catalyzing base in the presence of methanol, as reported in literature.[13]

The acid **13** reacted with the diol **15**[14] in the presence of DCC/DMAP to form the dumb-bell-type diester **16** (Scheme 4). The monoester **17** could be isolated separately. The diester **16** was also available by analogous esterification of monoester **17** with the acid **13**. MS (MALDI-TOF and HRFAB), NMR, IR, and UV spectra were obtained for compound **17**. The two fullerene C(sp^3) signals could not be observed in the ^{13}C-NMR spectrum of compound **17** due to the long relaxation times but all other signals were clearly detected. However, diester **16** was too insoluble to record a ^{13}C-NMR spectrum. The ^{1}H-NMR spectrum of compound **16** indicated two singlets consistent with the molecular symmetry. The MALDI-TOF mass spectrum showed the molecular ion peak and the $M^- - C_{60}$ peak. With this procedure, the fullerene and the cubane moiety were linked together, and it should be possible to combine other alcohols in this simple way with the acid **13**.



Scheme 4. Synthesis of **16** by twofold esterification

Conclusion

The addition of bifunctional nitrile oxides to C_{60} generated cycloadducts **2**, **4**, and **8a−b**, which can be regarded as building blocks of polyaddition polymers.

Having accomplished the synthesis of the new isoxazolo[4′,5′:1,2][60]fullerene-3′-carboxylic acid (**13**),[15] we now present a different strategy to build such dumb-bell structures employing twofold esterification with a diol. This has the advantage that a wide range of alcohols can be used. In this case the reaction was utilized to join the spherical fullerene structure with cubane, a combination of an archimedic with a platonic element.

We recently reported the ring opening of the heterocycle with the C-3′-unsubstituted isoxazolofullerene.[7] We now found that this ring opening can also be achieved by decarboxylation of the carboxylic acid **13**.

Furthermore we have evidence that compounds **8a−b** can be separated as two atropisomers due to steric hindrance between the bulky spacer and the two fullerene units. Even the less bulky 2-methoxy-9-anthryl group in the monoadduct **11** restricts free rotation of the substituent around the C-3′-anthryl single bond, which leads to axial chirality. Variation of bulky asymmetric reagents could form new key compounds to chiral fullerene adducts.

Experimental Section

General Remarks: NMR: Bruker AC 300 (300 MHz and 75 MHz, for ^{1}H and ^{13}C, respectively); chemical shifts are reported with respect to TMS. Calibration with solvent signals ([D_6]acetone: δ_H = 2.04, δ_C = 29.8; $CDCl_3$: δ_H = 7.24, δ_C = 77.0; [D_4]*o*-dichlorobenzene: δ_H = 7.07 [highfield signal], δ_C = 132.6 [lowfield signal]; 1-

chloronaphthalene: δ_C = 124.0 [highfield signal]). − Solid-state CPMAS ^{13}C NMR: Varian Unity Inova 400 (100.585 MHz, rotor spinning frequency 5 kHz, contact time 2 ms, proton high-power decoupling); chemical shifts are given with respect to TMS. Calibration with hexamethylbenzene $\delta_C(CH_3)$ = 17.3. − FT IR: Bruker IFS 66. − EI MS: VG ZAB-2F. − FAB MS: JOEL JMS-RSX 102A, positive-ion mode (matrix 3-nitrobenzyl alcohol/TFA, 99:1) and JOEL JMS-700, positive-ion mode (matrix nitrobenzyl alcohol). − MALDI-TOF MS: Bruker Biflex, negative-ion mode (matrix 9-nitroanthracene). − UV: HP 8452 (diode array). − Elemental analysis: Heraeus CHN-O-Rapid. − HPLC: Preparative column Buckyclutcher® I (250 mm × 21.1 mm, 10 μm, 100 Å), mobile phase toluene; silica gel (250 mm × 25 mm, 7 μm, 7 Å), mobile phase toluene; silica gel (250 mm × 30 mm, 5 μm, 60 Å), mobile phase toluene/acetonitrile, 9:1.

3′-[4-(Isoxazolo[4′,5′:1,2][60]fulleren-3′-yl)phenyl]isoxazolo-[4′,5′:1,2][60]fullerene (2): Dichlorodioxime **1** (4 mg, 2×10^{-5} mol) in 60 mL of toluene/diethyl ether (5:1, v/v) was added slowly during 1.5 h to a vigorously stirred solution of C_{60} (100 mg, 1.4×10^{-4} mol) in 1500 mL of toluene at room temperature. After the addition of triethylamine (3.6 mg, 3.5×10^{-5} mol), the stirring was continued for 15 h. The reaction mixture was concentrated to 500 mL and filtered directly without previous washing through a silica-gel column with toluene. The volume of the obtained solution was reduced to 250 mL, and finally the product was purified in portions of 4.5 mL on Buckyclutcher I[16] with HPLC yielding 80 mg of recovered C_{60} and 21 mg (1.5×10^{-5} mol, 78%) of the product as a fine brown powder. − ^1H NMR (300 MHz, [D_6]*o*-dichlorobenzene): δ = 8.72 (s). − ^{13}C NMR (75 MHz, 1-chloronaphthalene/[D_6]acetone, 9:1 [v/v]): δ = 78.25 (2 C, sp^3, fullerene), 104.79 (2 C, sp^3, fullerene), 133.41 (aromatic), 134.01 (aromatic), 136.13 (4 C), 136.59 (4 C), 139.55 (4 C), 139.68 (4 C), 140.82 (4 C), 141.19 (4 C), 141.34 (4 C), 141.43 (4 C), 141.58 (4 C), 141.62 (4 C), 141.93 (4 C), 141.99 (4 C), 142.08 (4 C), 143.13 (4 C), 143.46 (4 C), 143.52 (4 C), 143.59 (4 C), 143.82 (4 C), 144.26 (4 C), 144.38 (4 C), 144.43 (4 C), 144.80 (4 C), 144.84 (4 C), 145.07 (4 C), 145.12 (4 C), 145.39 (4 C), 145.43 (4 C), 145.49 (4 C), 146.39 (2 C), 146.90 (2 C), 152.73 (C=N). − FT IR (KBr): $\tilde{\nu}$ = 2963 cm^{-1} (m), 1608 (w, C=N), 1262 (s), 1096 (s), 1022 (s), 802 (s), 527 (w, C_{60}). − UV/Vis (1,2-dichlorobenzene): λ_{max} (lg ε) = 298 nm (4.63), 318 (4.67), 416 (3.72), 428 (3.59), 458 (3.51), 492 (3.46), 686 (3.14). − MALDI-TOF MS; *m/z* (%): 1602 (26) [M^-], 881 (26) [$M^- - C_{60}$], 720 (100) [C_{60}^-].

2-(Isoxazolo[4′,5′:1,2][60]fullerene-3′-carbonyloxy)ethyl Isoxazolo-[4′,5′:1,2][60]fullerene-3′-carboxylate (4): To a stirred solution of compound **3** (2 g, 3.8×10^{-3} mol) in 6 mL of water was added 0.65 mL of hydrochloric acid (d = 1.19 kg × dm^{-3}, 7.8×10^{-3} mol) at −5°C. A solution of $NaNO_2$ (530 mg, 7.6×10^{-3} mol) in 1 mL of water was added dropwise during a period of 10 min, and a second equivalent of HCl and $NaNO_2$ each was added in the same manner. The cooling was removed, and stirring was continued for 15 min. The reaction mixture was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried (Na_2SO_4), and the volume of the solution was reduced to 10 mL under vacuum. Of this slightly yellow solution, 0.5 mL was added in five portions to a stirred two-phase mixture of C_{60} (100 mg, 1.4×10^{-4} mol) in 250 mL of toluene and Na_2CO_3 (145 mg, 1.4×10^{-3} mol) in 20 mL of water during a period of 1 h. After this procedure, half of the C_{60} was used up (monitored by TLC, silica gel, toluene), and the toluene solution was brown. The organic layer was dried with Na_2SO_4, concentrated in vacuo, and the residue was purified by chromatography on a silica-gel column with toluene. The expected product **4** was eluted with R_f = 0.46, and the brown solid weighed 21 mg (1.3×10^{-5} mol, 19% based on employed C_{60}). The major product was identified as compound **5** (R_f = 0.26) yielding 15 mg (1.6×10^{-5} mol). − ^1H NMR (300 MHz, [D_4]*o*-dichlorobenzene): δ = 4.92 (s). − ^{13}C NMR (75 MHz, [D_4]*o*-dichlorobenzene): δ = 63.97 (CH_2), 75.66 (2 C, sp^3, fullerene), 106.90 (2 C, sp^3, fullerene), 136.80 (4 C), 137.18 (4 C), 140.27 (4 C), 140.31 (4 C), 141.77 (4 C), 141.87 (4 C), 142.23 (4 C), 142.33 (8 C), 142.44 (4 C), 142.49 (4 C), 142.80 (4 C), 142.86 (4 C), 142.89 (4 C), 143.44 (4 C), 144.14 (4 C), 144.17 (4 C), 144.38 (4 C), 145.17 (8 C), 145.23 (4 C), 145.76 (4 C), 145.96 (8 C), 146.35 (12 C), 146.97 (4 C), 147.19 (2 C), 147.40 (2 C), 147.78 (2 C), 159.59 (CO). − FT IR (KBr): $\tilde{\nu}$ = 2917 cm^{-1} (w, CH_2), 1728 (s, CO), 1584 (m), 1138 (s), 526 (s, fullerene). − UV/Vis (chloroform): λ_{max} (lg ε): 254 nm (4.51), 274 (4.42), 316 (4.11). − MALDI-TOF MS; *m/z* (%): 1640.5 (100) [M^-], 920.4 (32) [$M^- - C_{60}$], 720.3 (93) [C_{60}^-].

2-(Chloroacetoxy)ethyl Isoxazolo[4′,5′:1,2][60]fullerene-3′-carboxylate (5): ^1H NMR (300 MHz, CS_2/[D_6]acetone, 10:1 [v/v]): δ = 4.09 (s, 2 H, CH_2), 4.52 (m, 2 H, CH_2), 4.68 (m, 2 H, CH_2). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 40.69 (CH_2), 63.34 (CH_2), 63.88 (CH_2), 75.29 (1 C, sp^3, fullerene), 106.64 (1 C, sp^3, fullerene), 136.66 (2 C), 137.05 (2 C), 140.24 (2 C), 140.30 (2 C), 141.77 (2 C), 141.79 (2 C), 142.14 (2 C), 142.24 (2 C), 142.41 (2 C), 142.47 (2 C), 142.49 (2 C), 142.88 (2 C), 142.91 (4 C), 143.17 (2 C), 144.18 (2 C), 144.19 (2 C), 144.51 (2 C), 145.23 (2 C), 145.25 (2 C), 145.29 (2 C), 145.75 (2 C), 146.04 (4 C), 146.38 (2 C), 146.40 (2 C), 146.42 (2 C), 146.62 (2 C), 146.94 (1 C), 147.27 (1 C), 147.87 (1 C), 159.62 (CO), 167.15 (*C*OCH_2Cl). − MALDI-TOF MS; *m/z* (%) = 927.1 (100) [M^-], 720.0 (60) [C_{60}^-]. − FT IR (KBr): $\tilde{\nu}$ = 2921 cm^{-1} (w, CH), 1729 (s, CO), 1144 (s), 527 (s, fullerene). − UV/Vis (chloroform): λ_{max} (lg ε) = 254 nm (5.15), 316 (4.67). − HR FAB MS [$C_{66}H_6{}^{35}ClNO_5$]; *m/z*: calcd. 926.9935; found 926.9966.

1,1′-(2,3,6,7-Tetramethoxy-9,10-anthracenediyl)dicarbonitrile Dioxide (7): 1,1′-(2,3,6,7-tetramethoxy-9,10-anthracenediyl)dicarbaldoxime[17] (**6**), (2.19 g, 5.7×10^{-3} mol) and sodium ethoxide (617 mg, 1.14×10^{-2} mol) was dissolved in 20 mL of DMF. The red-brown solution was cooled down to 5−10°C. Within 20 min, 2.03 g of NBS, dissolved in 17 mL of DMF, was added to this solution. The reaction mixture was stirred for 30 min at 10°C and afterwards 50 mL of ice-cold water was added. After 12 h at 4°C, the crystals were filtered and washed with water. The yellow-orange solid was purified by flash chromatography with chloroform/methanol (95:5, v/v) on silica gel (R_f = 0.92). Light-sensitive orange crystals were obtained (10 mg, 2.6×10^{-5} mol, yield 0.5%). M.p. 156°C (decomposition). − ^1H NMR (300 MHz, $CDCl_3$): δ = 4.10 (s, 12 H, OCH_3), 7.15 (s, 4 H, aromatic). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.34 (OCH_3), 102.77 (CNO), 128.67, 133.98, 138.15, 152.06. − FT IR (KBr): $\tilde{\nu}$ = 3007 cm^{-1} (w, CH), 2934 (w, CH), 2286 (m, CN), 1529 (m), 1497 (s), 1455 (m), 1436 (m), 1420 (m), 1400 (m), 1277 (m), 1247 (s), 1204 (m), 1158 (m), 834 (m), 577 (m). − MS (EI, 70 eV); *m/z* (%): 380 (17) [M^+], 57 (37), 56 (29), 44 (100), 43 (50), 41 (37), 32 (39), 31 (45), 29 (57). − HR EI MS [$C_{20}H_{16}N_2O_6$]; *m/z*: calcd. 380.1008; found 380.1000.

3′-[10-(Isoxazolo-[4′,5′:1,2][60]fulleren-3′-yl)-2,3,6,7-tetramethoxy-9-anthryl]isoxazolo[4′,5′:1,2][60]fullerene (8a−b): C_{60} (75 mg, 1.04×10^{-4} mol, 20 equiv.) was dissolved in 250 mL of toluene under argon. A solution of **7** (2 mg, 5.26×10^{-6} mol) in 2 mL of chloroform was added. The mixture was stirred for 48 h and the resulting product mixture was purified by HPLC (Buckyclutcher). Apart from 68 mg (9.4×10^{-5} mol) of C_{60}, two other fractions were isolated: 0.7 mg (0.3×10^{-5} mol, 5.7%) of the minor fraction and 6 mg (2.6×10^{-5} mol, 49.4%) of the major fraction. − Minor fraction (eluted first): ^1H NMR (300 MHz, $CDCl_3$): δ = 4.00 (s,

12 H, OCH_3), 7.52 (s, 4 H, aromatic). − FT IR (KBr): $\tilde{\nu}$ = 2921 cm^{-1} (w, CH), 1493 (s), 1430 (m), 1243 (s), 1127 (m), 528 (w, fullerene). − MALDI-TOF MS; *m/z* (%): 1821.5 (39) [M^-], 1101.5 (20) [M^- − C_{60}], 719.8 (100) [C_{60}^-]. − Major fraction (eluted second): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.16 (s, 12 H, OCH_3), 7.78 (s, 4 H, aromatic). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.13 (4 C, OCH_3), 79.56 (2 C, sp^3, fullerene), 104.01 (aromatic), 111.92 (2 C, sp^3, fullerene), 126.65 (aromatic), 133.68 (aromatic) 135.31 (4 C), 136.10 (4 C), 140.26 (4 C), 140.33 (4 C), 141.41 (4 C), 141.71 (4 C), 141.75 (4 C), 142.10 (4 C), 142.37 (4 C), 142.48 (4 C), 142.69 (4 C), 142.87 (4 C), 142.96 (4 C), 143.89 (4 C), 144.21 (4 C), 144.36 (4 C), 144.42 (4 C), 144.78 (4 C), 144.87 (4 C), 144.90 (2 C), 145.02 (4 C), 145.14 (8 C), 145.53 (4 C), 145.78 (4 C), 145.96 (2 C), 146.00 (4 C), 146.20 (4 C), 146.29 (4 C), 146.36 (4 C), 150.32 (2 C, C=N), 150.35 (aromatic). − FT IR (KBr): $\tilde{\nu}$ = 2946 cm^{-1} (w, CH), 1493 (s), 1430 (m), 1242 (s), 1129 (m), 831 (m), 526 (s, fullerene). − UV/Vis (chloroform): λ_{max} (lg ε) = 232 nm (5.2), 256 (5.37), 318 (4.68), 360 (4.51), 388 (4.32), 422 (4.2), 430 (4.03). − MALDI-TOF MS; *m/z* (%): 1821.9 (32) [M^-], 1101.0 (17) [M^- − C_{60}], 720.1 (100) [C_{60}^-].

1-(2-Methoxy-9-anthryl)carbaldoxime (10): To a suspension of 1-(2-methoxy-9-anthryl)carbaldehyde[18] (**9**), (125 mg, 5.3 × 10^{-4} mol) in 6.5 mL of ethanol, was added hydroxylammonium chloride (780 mg, 1.13 × 10^{-2} mol, 21 equiv.), dissolved in 4 mL of water and neutralized with sodium carbonate. The reaction mixture was heated for 30 min at reflux. To the hot solution was added 60 mL of water, causing the precipitation of yellow crystals. The solid was filtered and washed with water. The crude product was purified by chromatography (chloroform, silica gel, R_f = 0.5) and dried in vacuo. A yellow powder (90 mg, 3.58 × 10^{-4} mol, 67.6%) with a melting point of 139°C was isolated. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.98 (s, 3 H, OCH_3), 7.20 (dd, J_{3-4} = 9.2 Hz, J_{3-1} = 2.4 Hz, 3-H), 7.43−7.57 (m, 6-H and 7-H), 7.69 (d, J_{1-3} = 2.4 Hz, 1-H), 7.92 (d, *J* = 9.3 Hz, 1 H, aromatic), 7.99 (d, *J* = 8.4 Hz, 1 H, aromatic), 8.38 (d, *J* = 8.7 Hz, 1 H, aromatic), 8.42 (s, 10-H), 9.19 (s, 1 H, CHN), OH signal not detected. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.34 (OCH_3), 101.31, 120.44, 121.13 (q), 124.33, 124.48, 126.96, 127.96 (q), 129.00, 129.48, 129.97 (q), 130.59, 130.86 (q), 149.37 (C=N), 158.54 (q, C_2). − FT IR (KBr): $\tilde{\nu}$ = 3330 cm^{-1} (OH), 3109 (w, CH), 3053 (w, CH), 2984 (w, CH), 1632 (s, C=N), 1468 (s), 1436 (m), 1270 (m), 1228 (vs, C−O), 1182 (m), 1065 (m), 1030 (m), 993 (m), 957 (m), 935 (m), 892 (s), 884 (m), 735 (s). − UV/Vis (chloroform): λ_{max} (lg ε) = 264 nm (5.05), 340 (3.74), 358 (3.87), 364 (3.89), 398 (3.92). − MS (EI, 70 eV); *m/z* (%): 250.8 (76) [M^+], 234.0 (55) [M^+ − OH], 218.9 (49) [M^+ − NOH], 189.9 (100), 163.0 (83), 164.0 (75), 125.3 (41), 87.9 (65), 81.1 (49). − $C_{16}H_{13}NO_2$ (251.28): calcd. C 76.48, H 5.21, N 5.57; found C 76.12, H 5.25, N 5.49.

3′-(2-Methoxy-9-anthryl)isoxazolo[4′,5′:1,2][60]fullerene (11): To a solution of **10** (80 mg, 3.2 × 10^{-4} mol) in 1.5 mL of DMF, was added sodium ethoxide (17.2 mg, 3.2 × 10^{-4} mol). The solution was cooled to 5°C, and NBS (56.8 mg, 3.2 × 10^{-4} mol), dissolved in 1 mL of DMF, was added. After stirring the mixture for 50 min at 10°C followed by the addition of 20 mL of ice-cold water, the yellow precipitate was filtered and washed with water. The crude yellow solid weighed 69 mg. To a solution of C_{60} (200 mg, 2.8 × 10^{-4} mol) in 400 mL of toluene was added 60 mg of the crude 1-(2-methoxy-9-anthryl)carbonitrile oxide, dissolved in 10 mL of chloroform. The mixture was stirred for 48 h and afterwards the solvent evaporated. The residue was purified by chromatography with toluene on silica gel (R_f = 0.6) leading to 42 mg (4.3 × 10^{-5} mol, 15.6% based on employed oxime **10**) of a black solid. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.07 (s, 3 H, OCH_3), 7.22 (d, *J* = 7.3 Hz, 1 H), 7.45−7.65 (m, 2 H, 6′-H and 7′-H), 7.76 (d, *J* = 2.2 Hz, 1 H, 1′-H), 7.95 (d, *J* = 9.2 Hz, 1 H), 8.03 (d, *J* = 8.5 Hz, 1 H), 8.51 (d, *J* = 9.2 Hz, 1 H), 8.54 (s, 1 H, 10′-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.54 (OCH_3), 79.01 (1 C, sp^3, fullerene), 102.24 (aromatic), 103.36 (1 C, sp^3, fullerene), 121.07, 124.89, 125.48, 127.32, 128.02, 128.23, 128.92, 129.04, 130.09, 130.29, 130.59, 131.69, 132.47 (all aromatic), 135.70 (1 C), 136.12 (1 C), 136.22 (1 C), 136.91 (1 C), 140.22 (1 C), 140.28 (1 C), 140.60 (1 C), 140.65 (1 C), 141.52 (1 C), 141.61 (1 C), 141.77 (1 C), 142.10 (1 C), 142.13 (1 C), 142.15 (1 C), 142.18 (1 C), 142.22 (1 C), 142.40 (2 C), 142.45 (1 C), 142.51 (1 C), 142.72 (2 C), 142.86 (2 C), 143.00 (2 C), 144.03 (2 C), 144.28 (1 C), 144.32 (1 C), 144.45 (1 C), 144.72 (1 C),144.90 (2 C), 144.95 (1 C), 145.07 (1 C), 145.15 (3 C), 145.18 (2 C), 145.26 (1 C), 145.31 (1 C), 145.46 (1 C), 145.53 (1 C), 145.73 (1 C), 145.87 (1 C), 145.91 (1 C), 146.01 (1 C), 146.03 (1 C), 146.29 (1 C), 146.31 (1 C), 146.35 (2 C), 146.40 (2 C), 147.23 (1 C), 147.85 (1 C), 153.54 (C=N), 158.25 (*C*OCH_3). − FT IR (KBr): $\tilde{\nu}$ = 2920 cm^{-1} (w, CH), 1628 (m), 1465 (m), 1228 (m, C−O), 1172 (m), 526 (s, fullerene). − UV/Vis (chloroform): λ_{max} (lg ε) = 234 nm (5.05), 258 (5.25), 318 (4.60), 348 (4.34), 360 (4.26), 390 (4.08) 416 (4.01). − HR FAB MS [$C_{76}H_{11}NO_2$]; *m/z*: calcd. 969.0789; found 969.0847.

4-(Isoxazolo[4′,5′:1,2][60]fulleren-3′-ylcarbonyloxymethyl)cubylmethyl Isoxazolo[4′,5′:1,2][60]fullerene-3′-carboxylate (16): To a stirred solution of the ester **12** (100 mg, 1.2 × 10^{-4} mol) in 200 mL of toluene under nitrogen was added trifluoromethanesulfonic acid (21 μL, 2.4 × 10^{-4} mol) at room temperature. The brown solution became colloidal immediately, and after 5 min no precursor **12** could be detected by TLC (silica gel, toluene). After the addition of 20 mL of water, the toluene phase was dried with $CaCl_2$ and filtered. The diol **15** (40 mg, 2.4 × 10^{-4} mol), DCC (50 mg, 2.4 × 10^{-4} mol), and DMAP (3 mg, 2.4 × 10^{-5} mol) were added and the stirred solution became clear after 5 min at room temperature. After the stirring was continued for 24 h, the mixture was concentrated under vacuum and filtered through a short silica-gel column with toluene to elute the product **16** (R_f = 0.41). Compound **17** was eluted with toluene/acetonitrile, 9:1 (v/v) (R_f = 0.46). Both products were purified with HPLC (silica gel, toluene). The yields for the brown products were 26 mg (1.5 × 10^{-5} mol, 25% based on employed ester **12**) for compound **16** and 30 mg (3.1 × 10^{-5} mol) for compound **17**. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.66 (s, 6 H, CH), 4.58 (s, 4 H, CH_2). − FT IR (KBr): $\tilde{\nu}$ = 2975 cm^{-1} (w, CH), 1739 (s, CO), 1138 (s), 527 (s, fullerene). − UV/Vis (chloroform): λ_{max} (lg ε) = 254 nm (5.15), 316 (4.69). − MALDI-TOF MS; *m/z* (%): 1743.4 (50) [M^-], 720.0 (100) [C_{60}^-].

4-(Hydroxymethyl)cubylmethyl [Isoxazolo[4′,5′:1,2][60]fullerenyl-3′-carboxylate (17): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.75 (m, 8 H, CH_2, CH), 4.63 (s, 2 H, CH_2), 1.23 (t, ^3J = 4 Hz, 1 H, OH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 43.89 (CH), 44.40 (CH), 56.08 (q), 59.26 (q), 63.53 (CH_2), 67.33 (CH_2), 136.65 (2 C), 137.01 (2 C), 140.17 (2 C), 140.32 (2 C), 141.78 (2 C), 141.83 (2 C), 142.18 (2 C), 142.44 (2 C), 142.47 (2 C), 142.49 (2 C), 142.51 (2 C), 142.88 (2 C), 142.92 (4 C), 143.45 (2 C), 144.16 (2 C), 144.24 (2 C), 144.56 (2 C), 145.25 (4 C), 145.34 (2 C), 145.68 (2 C), 146.05 (4 C), 146.38 (2 C), 146.43 (4 C), 146.65 (2 C), 147.30 (1 C), 147.35 (1 C), 147.95 (1 C), 159.84 (CO). − FT IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1} (m, OH), 2922 (s, CH), 1740 (s, CO), 1512 (s), 1151 (s), 527 (s, fullerene). − UV/Vis (chloroform): λ_{max} (lg ε) = 254 nm (4.99), 316 (4.51). − MALDI-TOF MS; *m/z* (%): 953.1 (100) [M^-], 720.0 (50) [C_{60}^-]. − HR FAB MS [$C_{72}H_{13}NO_5$]; *m/z*: calcd. 953.0688; found 953.0637.

Isoxazolo[4′,5′:1,2][60]fullerene-3′-carboxylic Acid (13): To isolate the acid **13**, the volume of the washed and dried colloidal toluene

solution (see preparation of compound **16**) was reduced to 5 mL. The product precipitated within 2 h at room temperature as brown crystals (80 mg, 10^{-4} mol, 86%). − Solid-state ^{13}C-CPMAS NMR (100 MHz): δ = 75.30 (sp^3, fullerene), 108.08 (sp^3, fullerene), 140.74−149.72 (sp^2, fullerene, imine), 168.42 (CO). − FT IR (KBr): $\tilde{\nu}$ = 3460 cm^{-1} (m, OH), 1691 (m, CO), 1180 (m), 527 (s, fullerene). − UV/Vis (DMSO): λ_{max} (lg ε) = 260 nm (5.11), 332 (4.81). − MALDI-TOF MS; *m/z* (%): 807.1 (20) [M^-], 762.1 (27) [M^- − COOH], 720.0 (100) [C_{60}^-].

1-Cyano-2-hydroxy-1,2-dihydro[60]fullerene (14): The ester **12** (36 mg, 4.2×10^{-5} mol) was dissolved in 100 mL of toluene under nitrogen. To the stirred solution was added *p*-toluenesulfonic acid monohydrate (30 mg, 1.6×10^{-4} mol), and the solution was heated at reflux for 9 h. After cooling to room temperature, the brown mixture was filtered through a short silica-gel column (solvent: toluene) to remove a small amount of C_{60} (byproduct) and traces of the unchanged ester **12**. The product was eluted with toluene/acetonitrile, 9:1 (v/v) (R_f = 0.50). HPLC analysis (silica gel; toluene/acetonitrile, 9:1) indicated a purity of 98.8% of the dark brown solid. The yield was 24% (7.5 mg, 10^{-5} mol). − Spectroscopic data are identical to the data reported previously.[7]

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