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Synthesis of 1,1′-Binaphthyl-Based Enantiopure C_{60} Dimers

Francesco Giacalone, José L. Segura, and Nazario Martín*

Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense, E-28040-Madrid, Spain

nazmar@quim.ucm.es

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Abstract: The first enantiomerically pure and soluble C_{60} dimers have been synthesized from suitably functionalized 1,1′-binaphthyl derivatives by 1,3-dipolar cycloaddition of the respective in situ generated diazo compounds to C_{60}. These systems exhibit optical and electrochemical activity.

The synthesis of enantiopure fullerenes is a topic that has received considerably less attention than the racemic preparation of fullerene derivatives, as a consequence of the spherical geometry of the C_{60} molecule. Nevertheless, different synthetic strategies have been developed for the preparation of C_{60}-based chiral monoadducts involving asymmetric[1] or C_2-symmetric[2] molecules. More recently, inherently asymmetric bisadducts of C_{60} with C_2-symmetry[3] or inherently asymmetric open-cage C_{60} derivatives[4] have been also used.

On the other hand, [60]fullerene dimers represent a new type of carbon allotropes that are of interest in different areas such as molecular electronic devices and in supramolecular chemistry.[5] However, to the best of our knowledge, chiral synthesis of fullerene dimers is a field that still remains unexplored.

In this paper, we report the synthesis and properties of optically active [60]fullerene dimers prepared from suitably functionalized enantiomerically pure 1,1′-binaphthyl derivatives. In this regard, the 1,1′-binaphthyl core has been used as an important building block for the preparation of more sophisticated systems[6] with applications in areas such as asymmetric catalysis,[7] molecular recognition,[8] nonlinear optics,[9] or photoluminescence.[10]

In our group, we have recently reported the use of 1,1′-binaphthyl derivatives for the preparation of intrinsically chiral polymers with a control on the conjugation length[10a,11] as well as in the preparation of new electroactive organic materials[12] and chiral and photoluminescent rigid dendrimers.[13] Recently, we have described the synthesis of new enantiomerically pure binaphthyl derivatives bearing triphenylphosphine, phosphonate, or formyl groups as useful synthetic building blocks.[14]

Now we have used the (*R*)-2,2′-didodecyloxy-6,6′-diformyl-1,1′-binaphthyl (**1**)[10a] for the preparation of the first optically active C_{60} dimers (**3** and **6**) (Scheme 1). A major problem in the synthesis of C_{60} dimers is the poor solubility they exhibit, thus preventing their spectroscopic and electrochemical characterization.[5] Therefore, the presence of long alkyl chains on the binaphthyl unit is important in order to enhance the solubility of the obtained dimeric fullerenes.

The synthesis of chiral dimer (*R*)-**3** was carried out by 1,3-dipolar cycloaddition of the diazo compound, generated in situ from tosylhydrazone derivative (*R*)-**2** under basic conditions,[15] to C_{60} in 9% yield (15% yield based on reacted C_{60}), together with the monoadduct (*R*)-**4** in 18% yield (30% yield based on reacted C_{60}). Compound (*R*)-**2** was in turn prepared from (*R*)-**1** by reaction with *p*-toluenesulfonylhydrazide in almost quantitative yield (97%).

To obtain a more flexible C_{60} dimer, we carried out the reduction of (*R*)-**1** to the dihydroxymethyl derivative (*R*)-**5** by using $LiAlH_4$ in good yield (91%). Further esterification of the diol (*R*)-**5** with the previously reported [6,6]-phenyl-C_{61}-butyric acid (PCBA)[16] by using DMAP and DCC in dry refluxing toluene led to the new C_{60} dimer (*R*)-**6** in 40% yield, and the monoadduct (*R*)-**7** in 23% yield. It is worth mentioning that both compounds were purified by chromatography [silica gel, cyclohexane first, and then, cyclohexane/ethyl acetate (98:2)] and further centrifugation in methanol.

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* To whom correspondence should be addressed. Fax: +34-913944103.

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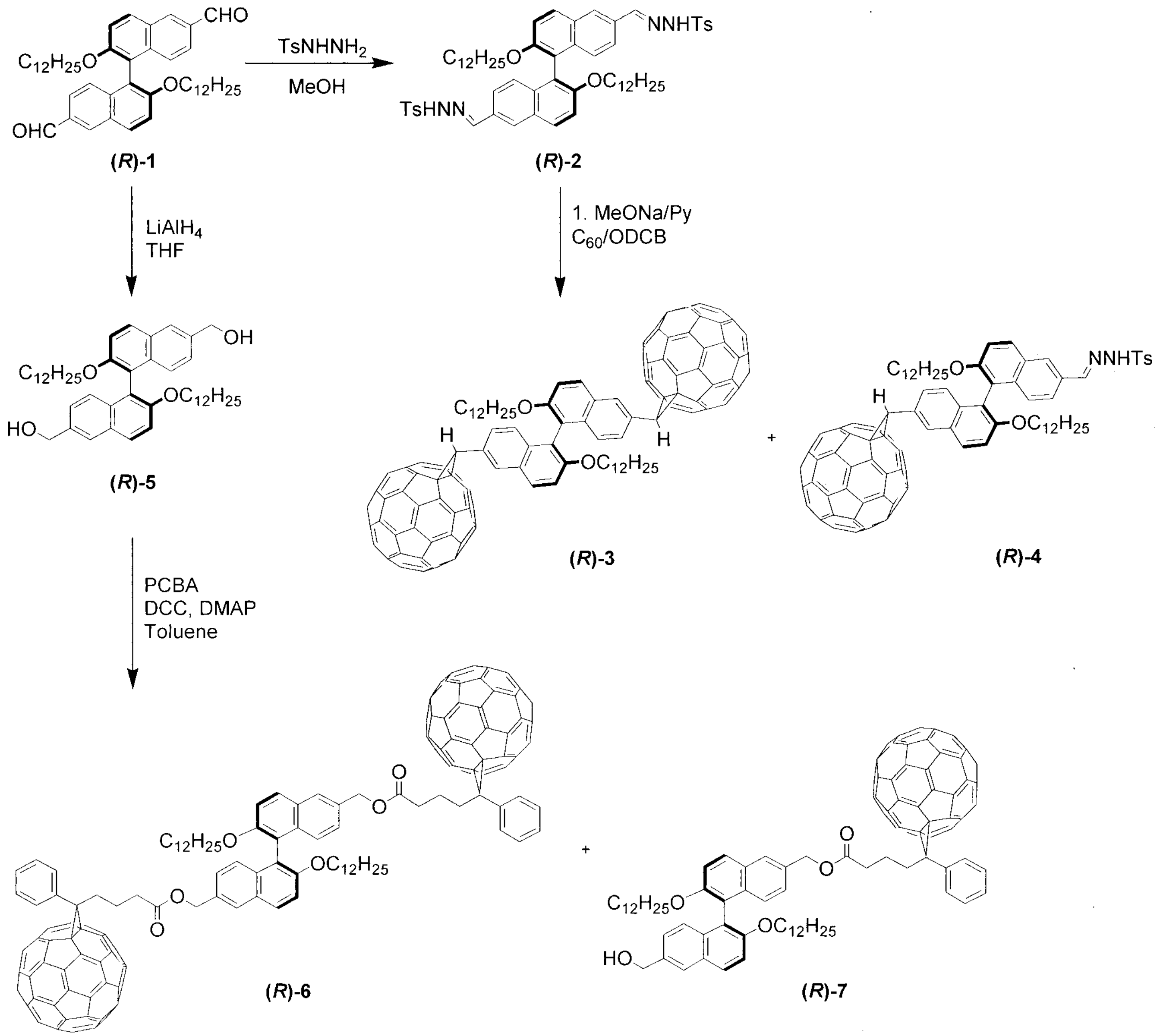
10.1021/jo020088u CCC: $22.00

Scheme 1



Both chiral dimers (*R*)-**3** and (*R*)-**6** were characterized analytically and spectroscopically (UV−vis; FTIR; ^{1}H and ^{13}C NMR, MS). Thus, the electronic spectra showed the low intensity band at around 430 nm characteristic of 1,2-dihydrofullerenes. The ^{1}H and ^{13}C NMR are totally consistent with the expected spectra, exhibiting signals for the fullerene sp^3 carbons at δ 75.75 and 69.76 for (*R*)-**3** and δ 79.86 and 69.63 for (*R*)-**6**. Confirmation of the structures was carried out by elemental analyses and ESI mass spectroscopy, which showed the molecular ions at *m*/*z* 2088 (M$^+$) for (*R*)-**3** and 2463 (M$^+$ + 23) for (*R*)-**6**.

Due to the absorption in the visible region, the optical rotation of the chiral C_{60} dimers prepared was difficult to determine in an accurate way. However, we were able to measure the circular dichroism (CD) spectra of both (*R*)-**3** and (*R*)-**6** enantiomerically pure compounds as depicted in Figure 1. In agreement with other previously reported CD spectra for substituted C_{60} derivatives,[17] almost flat lines were observed between 350 and 700 nm.

The structure of both chiral dimers was determined by using theoretical calculations at the semiempirical PM3 level. In agreement with previous references, torsion angles of ~75° were determined between both naphthalene units, thus preventing conjugation between them.

Interestingly, different geometries depending upon the relative position of both C_{60} units are possible for dimer (*R*)-**3**. Calculations show similar heats of formation for those geometries with the C_{60} units spatially separated (Figure 2). However, when the two C_{60} units are in a spatially close configuration (Figure 2c) the calculated geometry was ~13 kcal/mol less stable, as a consequence of the steric interaction between both C_{60} spheres, which are separated by a distance of 3.3 Å. This distance is slightly shorter than the sum of the van der Waals radii for two carbon atoms.[18]

The redox properties of the electroactive C_{60} dimers (*R*)-**3** and (*R*)-**6** were determined by cyclic voltammetry (CV) measurements at room temperature in *o*-DCB/MeCN (4:1) as solvent. The CV data show four reversible

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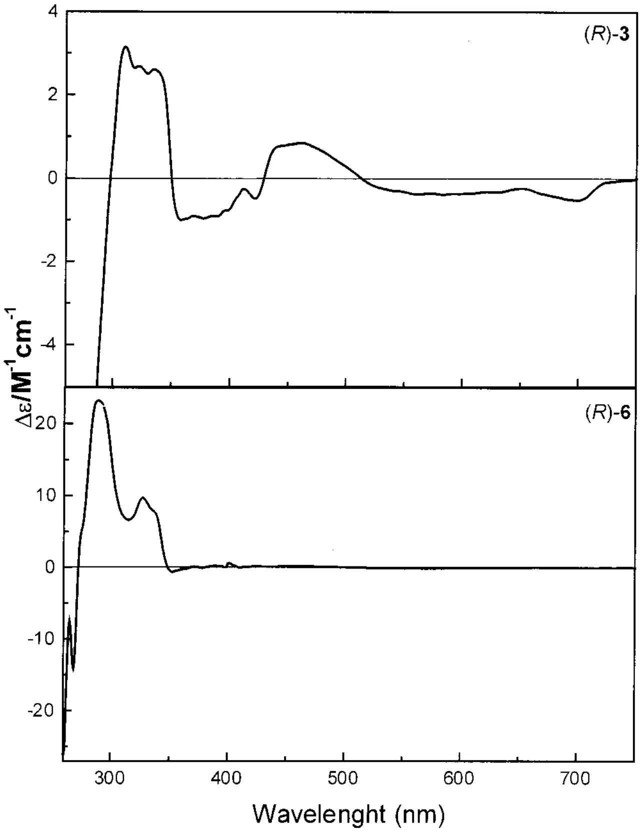

Figure 1. CD spectra of compounds (*R*)-**3** in $CHCl_3$ ($c = 0.307 \times 10^{-4}$ M, $d = 1$ cm, 25 °C) and (*R*)-**6** in CH_2Cl_2 ($c = 0.401 \times 10^{-4}$ M, $d = 1$ cm, 25 °C).

reduction waves corresponding to the reduction of the fullerene unit [(*R*)-**3**: $E^1_{red} = -0.69$ V, $E^2_{red} = -1.06$ V, $E^3_{red} = -1.56$ V, $E^4_{red} = -2.03$ V; (*R*)-**6**: $E^1_{red} = -0.67$ V, $E^2_{red} = -1.06$ V, $E^3_{red} = -1.56$ V, $E^4_{red} = -1.99$ V].

These data clearly show that both C_{60} units are reduced independently to form the respective anionic species. This finding is in agreement with that previously observed for other dimeric systems in which the covalently connected C_{60} units are not in close proximity.[5]

The reduction potentials are slightly shifted to more negative values than the parent C_{60} due to the saturation of a double bond on the C_{60} backbone, which raises the LUMO energy of these systems.[19]

On the oxidation side, an irreversible oxidation wave corresponding to the formation of the radical cation of the alkoxynaphthalene moiety was observed at 1.42 and 1.44 V for (*R*)-**3** and (*R*)-**5**, respectively. These data suggest that these electroactive acceptor–donor–donor–acceptor (A–D–D–A) species are appealing systems for further photophysical studies in the search of energy and electron-transfer processes. Work is currently in progress in this direction.

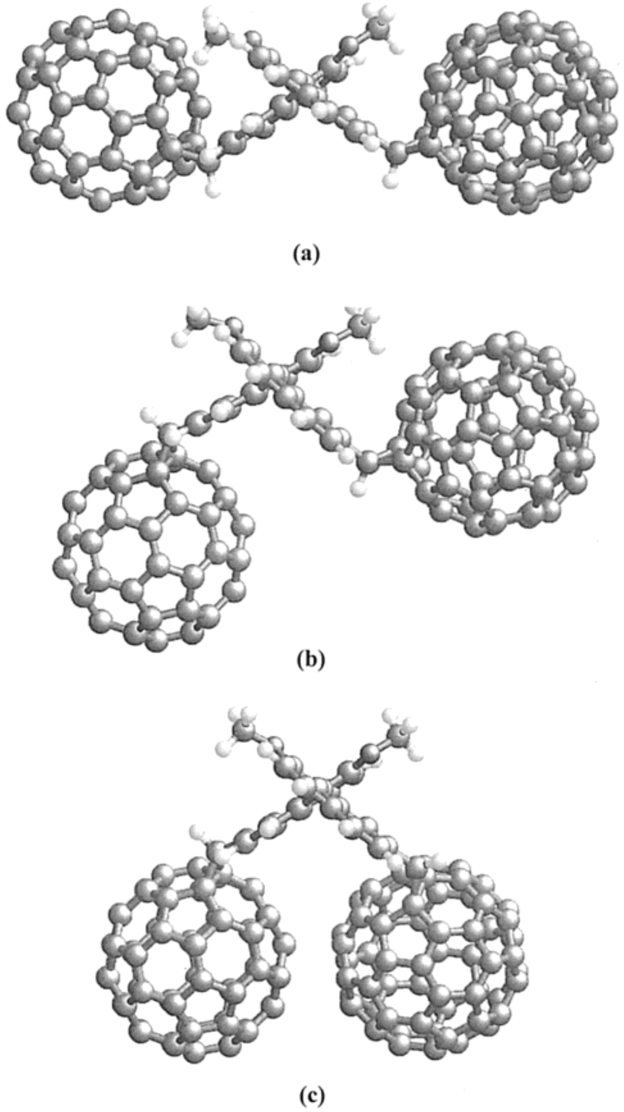

Figure 2. Molecular modeling of (*R*)-**3**: (a and b) with both C_{60} units spatially separated; (c) with both C_{60} units in close proximity. The $OC_{12}H_{25}$ groups in (*R*)-**3** have been replaced by OCH_3 groups for calculations.

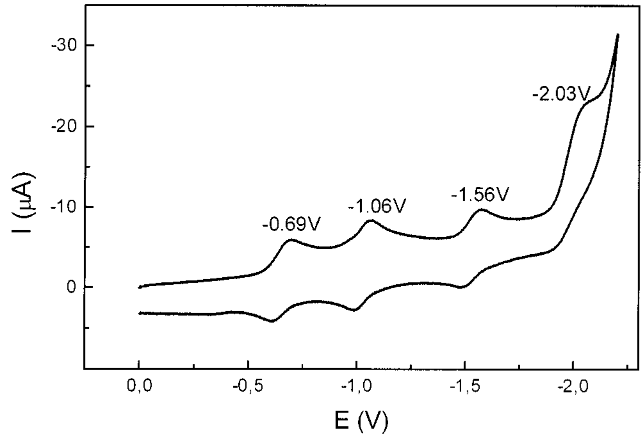

Figure 3. Cyclic voltammogram of (*R*)-**3** in *o*-DCB/MeCN (4:1) (0.1 M *n*-Bu_4NClO_4) at 100 $mV \cdot s^{-1}$; SCE as reference electrode and GCE as working electrode.

Experimental Section

All melting points were measured with a melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets or neat films. ^{13}C and ^1H NMR spectra were recorded with a 200 MHz for ^1H and 75 MHz for ^{13}C spectrometer or a 500 MHz for ^1H and 125 MHz for ^{13}C spectrometer. Chemical shifts are given as δ values (internal standard: TMS). [α_D] values were detemined using the light of a sodium lamp (λ = 589 nm), at room temperature, in a cylindrical cell with a length of 1 dm and a volume of 1 mL. Semiempirical calculations (PM3) were performed using the program Hyperchem Pro (version 5.1)

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from Hypercube, Inc., with a PC compatible at 1000 MHz. For each structure, the minimum energy was determined after reminimization. Cyclic voltammograms were recorded on a potentiostat/galvanostat AUTOLAB with PGSTAT30 equipped with a software GPES for Windows version 4.8. The electrochemical analysis have been carried out using a GCE (glassy carbon) as working electrode, SCE as reference electrode, Bu_4NClO_4 as supporting electrolyte, and *o*-dichlorobenzene/acetonitrile (ratio 4:1) as solvent at a scan rate of 200 mV/s. Circular dichroism was carried out in a spectropolarimeter equipped with 150 W xenon lamp. Pyridine was dried with calcium hydride.

(*R*)-2. A mixture of (*R*)-2,2′-didodecyloxy-6,6′-diformyl-1,1′-binaphthalene(100 mg, 0.15 mmol) and *p*-toluenesulfonyl hydrazide (66 mg, 0.35 mmol) suspended in 5 mL of dry methanol was stirred and refluxed during 5.5 h. The mixture was left without heating during 1 day, and then after vacuum evaporation of the solvent, the orange solid obtained was chromatographically purified (silica gel, hexane/diethyl ether (3:7)) to yield 143 mg (97%) of yellow-green solid. Mp: 56−59 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.92 (d, 2H, $J = 9$ Hz), 7.76 (d, 4H, $J = 8.2$ Hz), 7.68 (d, 4H, $J = 2.5$ Hz), 7.44 (d, 2H, $J = 9$ Hz), 7.42 (dd, 2H; $J_1= 9$ Hz, $J_2= 1.2$ Hz), 7.18 (d, 4H, $J = 8.2$ Hz), 6.82 (d, 2H, $J = 9$ Hz), 3.98 (t, 4H, $J = 6.4$ Hz), 2.32 (s, 6H), 1.43 (t, 6H, $J = 7$ Hz), 1.25−1.01 (m, 34H), 0.88 (t, 6H, $J = 7$ Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.65, 148.10, 144.16, 135.33, 135.04, 129.58, 129.43, 128.58, 128.45, 127.89, 120.24, 115.93, 69.67, 31.93, 29.68, 29.65, 29.63, 29.48, 29.36, 29.28, 29.14, 25.65, 22.69, 21.51, 16.63, 14.12. IR (KBr): 3194, 3020, 2927, 2854, 1624, 1589, 1465, 1215, 1167, 1055, 758. MS (ESI): 1038 (M + Na$^+$), 1015 (M$^+$), 869, 722, 385, 301. Anal. Calcd for $C_{60}H_{78}N_4O_6S_2$: C, 70.97; H, 7.74. Found: C, 70.87; H, 8.01.

Methanofullerene (*R*)-3. To a suspension of (*R*)-**2** (105 mg, 0.11 mmol) in 6 mL of dry pyridine, NaOMe (21 mg, 0.22 mmol) was added, and the mixture was stirred for 15 min. A solution of 80 mg (0,10 mmol) of C_{60} in 5 mL of HPLC-grade 1,2-dichlorobenzene was added, and the mixture was stirred for 2.5 h. After vacuum removal of solvent, a dark solid was obtained that was chromatographed (silica gel, first with cyclohexane, then with cyclohexane/toluene (9:1)). After the solid was transferred in a centrifuge tube and suspended in MeOH, the mixture was immersed in a ultrasound bath for 1 min, the suspension was centrifugated, and the supernatant was decanted and treated twice in the same manner. The residue was dried in vacuo at 70 °C to yield 10 mg (mp > 300 °C) (9%, or 15% based on converted C_{60}) of a brown solid and 30 mg of monoaduct (*R*)-**4** (18%, or 30% based on converted C_{60}) as a brown solid (mp 142−144 °C). (*R*)-**3**: ^{1}H NMR δ ($CDCl_3$, 500 MHz): 8.43 (s, 2H), 8.08 (d, 2H), 7.86 (dd, 2H, $J = 1.5$ Hz), 7.47 (d, 2H), 7.17 (d, 2H), 5.43 (s, 2H), 3.95 (m, 4H), 1.38 (m, 4H), 1.18−0.89 (36H), 0.80 (t, 6H, $J = 3.7$ Hz). ^{13}C NMR δ ($CDCl_3$, 125 MHz): 155.17, 149.91, 147.83, 147.79, 145.72, 145.67, 145.60, 145.19, 145.16, 145.11, 145.07, 144.81, 144.68, 144.51, 144.41, 144.37, 144.12, 143.74, 143.69, 143.08, 142.99, 142.96, 142.91, 142.73, 142.35, 142.13, 142.09, 141.05, 140.84, 140.82, 138.57, 136.41, 133.90, 130.61, 129.50, 129.02, 128.90, 128.56, 128.21, 127.83, 126.38, 125.27, 120.47, 116.29, 75.75, 69.76, 43.65, 43.44, 31.98, 31.91, 30.16, 29.85, 29.78, 29.69, 29.64, 29.47, 29.35, 29.31, 29.22, 26.88, 25.65, 22.74, 22.68, 14.18, 14.11. FT-IR ν (KBr): 2920, 2850, 2359, 1629, 1461, 1242, 1022, 574, 525. MS *m/z* (ESI): 2087 (M$^+$). Anal. Calcd for $C_{166}H_{62}O_2$: C, 95.48; H, 2.99. Found: C, 93.83; H, 3.37.

(*R*)-4. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.35 (s, 1H), 8.01 (d, 1H, $J = 9$ Hz), 7.84 (m, 2H), 7.71 (m, 5H), 7.44 (d, 2H, $J = 9$ Hz), 7.35 (d, 1H, $J = 9$ Hz), 7.14 (d, 2H, $J = 8$ Hz), 7.05 (d, 1H, $J = 9$ Hz), 5.41 (s, 1H), 3.92 (m, 4H), 2.26 (s, 3H), 1.65 (m, 4H), 1.36 (t, 6H, $J = 6$ Hz), 1.33−0.85 (m, 30H), 0.81 (t 6H, $J = 6$ Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.87, 155.10, 149.87, 148.69, 147.80, 145.69, 145.58, 145.18, 145.07, 144.81, 144.68, 144.50, 144.37, 144.20, 144.12, 143.83, 143.69, 143.42, 143.17, 143.07, 142.96, 142.71, 142.37, 142.13, 142.08, 141.75, 141.05, 140.83, 138.54, 136.41, 135.51, 135.33, 135.25, 133.75, 130.64, 129.92, 129.61, 128.88, 128.59, 128.30, 127.93, 126.05, 123.24, 120.46, 120.18, 116.37, 115.80, 69.91, 69.48, 65.56, 53.74, 43.57, 31.98, 31.93, 29.82, 29.77, 29.65, 29.50, 29.37, 29.17, 25.61, 22.71, 21.60, 19.17, 14.14. IR (KBr): 3442, 2921, 2850, 1730, 1645, 1462, 1235, 1165, 525. MS (ESI): 1574 (M + Na$^+$), 1418.

Methanofullerene (*R*)-6. To a stirred mixture of PCBA (120 mg, 0.13 mmol), DMAP (35 mg, 0.26 mmol), and DCC (60 mg, 0.26 mmol) in 10 mL of dry toluene, under argon atmosphere, was added a solution of (*R*)-6,6′-bis(hydroxymethyl)-2,2′-didodecyloxy-1,1′-naphthalene (45 mg, 0.066 mmol) in 5 mL of dry toluene and refluxed during 16 h. The solvent was vacuum evaporated, and the solid residue was chromatographed (silica gel, cyclohexane first, cyclohexane/ethyl acetate 98:2). After transfer to a centrifuge tube and suspension in MeOH, the mixture was immersed in a ultrasound bath for 1 min, the suspension was centrifugated, and the surnatant was decanted and treated twice in the same manner. The residue was dried in vacuo at 70 °C to yield 63 mg (40%) of a dark brown solid (mp 155−157 °C) and 24 mg of (*R*)-**7** (23%) as a black solid (mp = 102−104 °C). (*R*)-**6**: ^{1}H NMR (500 MHz): δ 7.81 (m, 6H), 7.70 (t, 2H), 7.40 (m, 3H), 7.32 (m, 3H, $J = 7.5$ Hz), 7.27 (t, 2H, $J = 7.5$ Hz), 7.03 (d, 4H, $J = 5.8$), 5.11 (d, 4H), 3.83 (t, 4H), 2.81 (m, 1H), 2.47 (t, 1H, $J = 6.7$ Hz), 2.08 (t, 4H, $J = 6.7$ Hz), 1.64−1.52 (m, 8H), 1.42−0.99 (m, 38H), 0.81 (t, 6H, $J = 3.7$ Hz). ^{13}C NMR δ (125 MHz): 172.92, 172.81, 154.90, 148.77, 147.71, 147.32, 146.35, 145.77, 145.12, 145.06, 145.01, 144.76, 144.71, 144.65, 144.47, 144.33, 144.21, 143.97, 143.91, 143.71, 143.58, 143.53, 143.06, 143.01, 142.95, 142.87, 142.69, 142.52, 142.43, 142.19, 142.07, 141.90, 141.84, 141.24, 140.96, 140.68, 140.36, 139.76, 139.67, 138.75, 138.28, 138.12, 137.98, 137.87, 137.50, 136.64, 135.00, 133.89, 132.05, 130.70, 130.58, 129.25, 128.77, 128.65, 128.41, 128.21, 127.71, 127.57, 126.16, 126.02, 120.33, 116.00, 79.86, 69.63, 66.65, 66.54, 60.93, 51.83, 43.44, 35.27, 34.18, 33.61, 31.8, 30.16, 29.68, 29.50, 29.38, 29.32, 29.15, 26.88, 25.64, 22.71, 22.44, 19.96, 14.16. FT-IR ν (KBr): 2920, 2850, 1731, 1630, 1462, 1147, 698, 572, 525. MS *m/z* (ESI): 2463 (M$^+$ + 23), 2236, 2104, 1978, 1886, 1645. Anal. Calcd for $C_{188}H_{86}O_6$: C, 92.52; H, 3.55. Found: C, 91.15; H, 4.32.

(*R*)-7. ^{1}H NMR (500 MHz): δ 7.83 (t, 4H, $J = 9$ Hz), 7.72 (d, 2H, $J = 25$ Hz), 7.41 (m, 2H, $J = 7$ Hz), 7.33 (d, 2H, $J = 9$ Hz), 7.28 (t, 1H, $J = 7$ Hz), 7.12 (q, 1H, $J = 7$ Hz), 7.03 (s, 3H), 5.1 (d, 2H, $J = 32$ Hz), 4.67 (d, 2H, $J = 38$ Hz), 3.84 (m, 4H), 2.10 (t, 2H, $J = 7$ Hz), 1.64−1.53 (m, 6H), 1.43−1.27 (m, 10H), 1.22−0.86 (m, 28H), 0.81 (t, 3H, $J = 7$ Hz. ^{13}C NMR (125 MHz): δ 172.83, 154.94, 154.68, 154.80, 147.75, 147.33, 146.35, 145.13, 144.68, 144.47, 144.21, 143.91, 143.71, 143.61, 143.53, 142.97, 142.70, 142.54, 142.09, 141.90, 141.83, 141.26, 140.97, 140.69, 140.39, 139.78, 139.69, 138.76, 139.30, 138.13, 138.02, 137.88, 137.52, 136.65, 135.02, 133.95, 133.71, 132.05, 130.71, 130.55, 129.11, 129.03, 128.78, 128.63, 128.40, 128.20, 127.70, 127.56, 120.50, 120.39, 116.01, 69.63, 66.55, 65.59, 60.94, 43.45, 35.27, 34.14, 33.62, 31.93, 30.16, 29.67, 29.51, 29.37, 29.16, 26.90, 25.64, 22.70, 19.93, 14.13. FT-IR (KBr): 3420, 2921, 2850, 1732, 1596, 1462, 1265, 1152, 525 MS (ESI): 1561. Anal. Calcd for $C_{117}H_{76}O_5$: C, 89.97; H, 4.90. Found: C, 88.40; H, 5.27.

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Note Added after ASAP. The version of this paper posted on April 17, 2002, had incorrect compound numbering and experimental data. The correct version was posted on April 19, 2002.

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