Supplementary Material (ESI) for Chemical Communications

Supplementary data

Regio- and stereoselective synthesis of enantiomerically pure [60]fullerene trisadducts with an inherently chiral *e,e,e* addition pattern

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(4*R*,5*R*)-4,5-*O*-Isopropylidene-4,5-dihydroxy-2,6-octadiene-dioate (+)-1: The synthesis was performed according to the literature: S. Takano, A. Kurotaki, K. Ogasawara, *Synthesis*, 1987, 1075.

(4*R*,5*R*)-4,5-*O*-Isopropylidene-4,5-dihydroxy-2,6-octane-dioate (+)-2: A solution of **(+)-1** (1.60 g, 5.3 mmol) in EtOAc (50 ml) and a catalytic amount of 10% Pd/C was stirred for 12 h at room temperature in the presence of hydrogen atmosphere. The mixture was filtered through Celite and the solvent was evaporated under reduced pressure. **(+)-2** was isolated as a colourless oil (1.62 g, 100%). $[\alpha]_D^{22}$ (c = 0.0024 g ml^{-1}, $CHCl_3$) = +31°. δ_H($CDCl_3$, 300 MHz) 1.23 (t, 6H, J = 7.1 Hz), 1.33 (s, 6H), 1.75 (m, 2H), 1.90 (m, 2H), 2.44 (m, 4H), 3.61 (m, 2H), 4.11 (q, 4H, J = 7.1 Hz). δ_C($CDCl_3$, 75 MHz) 14.20, 27.19, 27.73, 30.65, 60.41, 79.55, 108.43, 173.15. MS (FAB, NBA), *m/z*: 303 ([M^+ + 1], 30%), 287([M^+ − 15], 100%).

(4*R*,5*R*)-4,5-Bis(3-hydroxy-propyl)-2,2-dimethyl-1,3-dioxolan (+)-3: This was prepared from **(+)-2** (1.60 g, 5.3 mmol) by $LiAlH_4$ reduction in dry THF, in the usual manner. Diol **(+)-3** was isolated as colourless high viscous oil (1.12 g, 97%). $[\alpha]_D^{25}$ (c = 0.0033 g ml^{-1}, $CHCl_3$) = +28.4°. δ_H($CDCl_3$, 300 MHz) 1.36 (s, 6H), 1.53 (m, 2H), 1.70 (m, 6H), 2.30 (s, 2H, OH), 3.60–3.70 (m, 6H). δ_C($CDCl_3$, 75 MHz) 27.63, 29.74, 29.88, 62.99, 81.28, 108.67. MS (FAB, NBA), *m/z*: 219 ([M^+ + 1], 72%), 203 ([M^+ − 15], 100%).

Synthesis of the *cyclo*-malonates (+)-4, (+)-5 and (+)-6: In a dry 1L round-bottomed flask equipped with gas inlet, 500 ml dropping funnel, and magnetic stirrer, **(+)-3** (1.7 g, 7.8 mmol, 1.00 equiv.) was dissolved under

nitrogen in dry CH_2Cl_2 (400 ml) followed by the addition of pyridine (1.25 ml, 15.6 mmol, 2.00 equiv.). Subsequently, a solution of malonyl dichloride (1.51 ml, 15.6 mmol, 2.00 equiv.) in dry CH_2Cl_2 (200 ml) was added dropwise over a period of 3 hours. After stirring for 1 day at room temperature the mixture was concentrated with rotary evaporator and filtered over a silica plug (6 × 6 cm) with CH_2Cl_2/EtOAc 50:50 to remove polymeric material and pyridine salts. The solution was evaporated and the crude product separated by flash column chromatography on silica gel using a mixture of CH_2Cl_2/EtOAc 70:30 as eluent. The order of elution was **(+)-4**, **(+)-5**, and **(+)-6**.

Compound **(+)-4**: Yellowish oil (156 mg, 7%). $[\alpha]_D^{24}$ (c = 0.0098 g ml^{-1}, $CHCl_3$) = +19.9°. δ_H($CDCl_3$, 300 MHz) 1.31 (s, 6H), 1.55 (m, 2H), 1.72–1.85 (m, 6H), 3.34 (s, 2H), 3.64 (br s, 2H), 4.09–4.25 (m, 4H). δ_C($CDCl_3$, 75 MHz) 22.84, 27.20, 27.59, 42.69, 65.09, 78.19, 108.53, 166.71. MS (FAB, NBA), *m/z*: 285 ([M^+ − 1], 15%), 271 ([M^+ − 15], 100%).

Compound **(+)-5**: White solid (320 mg, 7.1%), m.p. 134.8 °C. $[\alpha]_D^{24}$ (c = 0.0011 g ml^{-1}, $CHCl_3$) = +25°. δ_H($CDCl_3$, 300 MHz) 1.31 (s, 12H), 1.48 (m, 4H), 1.58–1.82 (m, 12H), 3.32 (s, 4H), 3.55 (m, 4H), 4.14 (m, 8H). δ_C($CDCl_3$, 75 MHz) 25.64, 27.63, 29.13, 42.04, 65.41, 80.44, 108.69, 166.90. MS (FAB, NBA), *m/z*: 573 ([M^+ + 1], 30%), 557 ([M^+ − 15], 58%), 457 ([M^+ − 115], 100%).

Compound **(+)-6**: Colourless oil (120 mg, 1.8%). $[\alpha]_D^{24}$ (c = 0.0020 g ml^{-1}, $CHCl_3$) = +20°. δ_H($CDCl_3$, 300 MHz) 1.34 (s, 18 H), 1.45–1.68 (m, 12H), 1.70–1.91 (m, 12H), 3.36 (s, 6H), 3.58 (m, 6H), 4.17 (m, 12H). δ_C($CDCl_3$, 75 MHz) 25.59, 27.66, 29.28, 41.90, 65.56, 80.49, 108.63, 166.96. MS (FAB, NBA), *m/z*: 843 ([M^+ − 15], 68%).

Reaction of C_{60} with macrocycle (+)-5 to give 7 and 8: In a dry 500 ml two-necked flask equipped with a gas inlet, dropping funnel, and magnetic stirrer, C_{60} (144 mg, 0.2 mmol) was dissolved in toluene (200 ml) under argon. Subsequently, the macrocycle **(+)-5** (103 mg, 0.18 mmol) and iodine (91.5 mg, 0.36 mmol) were added, followed by the dropwise addition of a solution of DBU (107.4 µl, 0.72 mmol) in toluene (100 ml) over a period of 2 hours. The solution was stirred at room temperature for 1 day. The crude reaction mixture was filtered through a paper filter and chromatographed on a SiO_2 column (6 × 25 cm). Traces of C_{60} and other

impurities were eluted with toluene, and then the eluent was changed to toluene/EtOAc 80:20. Two fractions were obtained. The first consisted of the bis-fullerene adduct **8**, whereas the second was the *cis*-2 bisadduct **7**.

Compound **7**: 80 mg, 34.5%. δ_H($CDCl_3$, 400 MHz) 1.31 (s, 3H), 1.36 (s, 3H), 1.38 (s, 3H), 1.41 (s, 3H), 1.51–1.97 (m, 16H), 3.39 (ddd, J = 8.6, 8.6, 1.8 Hz, 1H), 3.59 (ddd, J = 8.7, 8.7, 1.3 Hz, 1H), 3.88 (m, 2H), 4.30 (m, 2H), 4.37–4.61 (m, 5H), 4.81 (ddd, J = 10.4, 10.4, 3.2 Hz, 1H). δ_C($CDCl_3$, 100 MHz) 24.42, 24.99, 25.43, 27.18, 27.22, 27.34, 27.66, 28.24, 28.47, 50.05, 50.17, 65.38, 65.60, 66.37, 67.60, 67.66, 70.12, 70.60, 77.68, 78.60, 78.88, 79.58, 108.34, 108.81, 135.08, 135.43, 135.90, 136.77, 136.85, 137.10, 138.99, 140.90, 141.05, 141.08, 141.37, 141.49, 141.85, 142.25, 142.78, 143.42, 143.62, 143.68, 144.12, 144.18, 144.27, 144.42, 144.47, 144.77, 144.94, 145.07, 145.27, 145.33, 145.47, 145.66, 145.82, 145.91, 146.07, 146.23, 146.39, 147.29, 147.38, 147.44, 148.67, 162.95, 163.42, 163.52, 164.00. UV/Vis ($CHCl_3$): λ_{max}/nm (ε/$dm^3mol^{-1}cm^{-1}$) 255 (154 000), 323 (53 000), 380 (13 500, sh), 438 (3980). MS (FAB, NBA), *m/z*: 1288 ([M^+], 50%), 720 ([C_{60}^+], 100%).

Compound **8**: 30 mg, 8.3%. δ_H($CDCl_3$, 400 MHz) 1.41 (s, 12H), 1.70 (m, 4H), 1.82 (m, 4H), 1.99 (m, 4H), 2.11 (m, 4H), 3.72 (m, 4H), 4.54 (m, 8H). δ_C($CDCl_3$, 100 MHz) 25.67, 27.40, 29.26, 51,87, 67.05, 71.43, 80.36, 108.76, 139.10, 140.97, 141.88, 142.19, 142.99, 143.02, 143.09, 143.45, 143.87, 144.63, 144.68, 144.89, 145.09, 145.19, 145.27, 145.50, 163.57. UV/Vis ($CHCl_3$): λ_{max}/nm (ε/$dm^3mol^{-1}cm^{-1}$) 259 (323 000), 328 (106 000), 425 (7800). MS (FAB, NBA), *m/z*: 2009 [M^+], 720 [C_{60}^+].

Reaction of C_{60} with macrocycle (+)-6 to give 9, (+)-10a and (−)-10b: In a dry 250 ml two-necked flask equipped with a gas inlet, dropping funnel, and magnetic stirrer, C_{60} (96 mg, 0.13 mmol, 1.00 equiv.) was dissolved in toluene (150 ml) under argon. Subsequently, the macrocycle **(+)-6** (102 mg, 0.12 mmol, 0.9 equiv.) and iodine (91.5 mg, 0.36 mmol, 2.7 equiv.) were added, followed by the dropwise addition of a solution of DBU (147.6 µl, 0.99 mmol, 7.5 equiv.) in toluene (60 ml) over a period of 2 hours. The solution was stirred at room temperature for 1 day. The crude reaction mixture was filtered through a paper filter and chromatographed on a SiO_2 column (6 × 25 cm). Traces of C_{60} and other impurities were eluted with toluene, and then the eluent was changed to toluene/EtOAc 80:20. Three fractions were obtained. The first consisted of the trisadduct **9**, whereas the second and the third consisted of trisadducts **(+)-10a** and **(−)-10b**, respectively.

Compound **9**: Olive-green solid (2.7 mg, 1.4%). R_f (SiO_2, toluene/EtOAc 80:20) = 0.37. δ_H($CDCl_3$, 400 MHz) 1.32 (s, 9H), 1.34 (s, 9H), 1.40 (m, 12H), 1.85 (m, 12H), 3.44 (ddd, J = 8, 8, 2.8 Hz, 3H), 3.56 (ddd, J = 8.7, 8.7, 2 Hz, 3H), 4.42 (m, 6H), 4.60 (m, 6H). δ_C($CDCl_3$, 100 MHz) 24.83, 25.19, 27.23, 27.33, 29.99, 30.17, 50.47, 67.74, 68.34, 70.44, 71.30, 78.77, 79.73, 108.19, 134.38, 134.82, 139.64, 139.96, 141.63, 142.30, 142.40, 142.57, 142.60, 143.14, 143.53, 144.72, 144.90, 145.60, 145.65, 147.80, 164.66, 164.80. UV/Vis ($CHCl_3$): λ_{max}/nm (ε/$dm^3mol^{-1}cm^{-1}$) 268 (89 360, sh), 313 (43 720), 335 (40 400), 469 (2800) 623 (880), 683 (790). MS (FAB, NBA), *m/z*: 1573 ([M^+], 16%) 720 ([C_{60}^+], 100%).

Compound **(+)-10a**: Cherry-red solid (19.1 mg, 10.1%). R_f (SiO_2, toluene/EtOAc 80:20) = 0.32. $[\alpha]_D^{22}$ (c = 0.00012 g ml^{-1}, $CHCl_3$) = +1275°. δ_H($CDCl_3$, 400 MHz) 1.31 (s, 9H), 1.32 (s, 9H), 1.51 (m, 9H), 1.76 (m, 12H), 1.99 (m, 3H), 3.33 (m, 3H), 3.56 (ddd, J = 9.6, 9.6, 2 Hz, 3H), 4.22 (m, 6H), 4.45 (ddd, J = 10.3, 10.3, 2.5 Hz, 3H), 4.65 (ddd, J = 11.4, 7.4, 3.8 Hz, 3H). δ_C($CDCl_3$, 100 MHz) 25.26, 25.54, 27.09, 27.21, 27.96, 28.75, 54.34, 66.60, 67.38, 70.64, 71.19, 79.32, 80.31, 107.72, 140.70, 141.12, 141.45, 142.43, 143.10, 143.74, 143.98, 144.41, 144.64, 145.22, 145.66, 146.32, 146.49, 146.63, 146.79, 147.88, 162.64, 162.96. UV/Vis ($CHCl_3$): λ_{max}/nm (ε/$dm^3mol^{-1}cm^{-1}$) 251 (55 000), 281 (47 930), 303 (40 050, sh), 380 (4910), 484 (4560), 563 (1290). CD ($CHCl_3$): 254 nm ($\Delta\varepsilon$ = −37.7), 289.2 (+17.1), 301 (−2.5), 311.2 (+13.6), 328.8 (−5.2), 356.2 (+13.5), 379.6 (−7.3), 385.4 (−5.7), 394.4 (−7.9), 456.2 (−4.1), 470.2 (−2.8), 485.8 (−4.6), 514.8 (+5.4), 560.6 (+13.7). MS (FAB, NBA), *m/z*: 1574 ([M^+ + 1], 100%), 720 ([C_{60}^+], 71%).

Compound **(−)-10b**: Cherry-red solid (73.8 mg, 39.1%). R_f (SiO_2, toluene/EtOAc 80:20) = 0.24. $[\alpha]_D^{23}$ (c = 0.00011 g ml^{-1}, $CHCl_3$) = −1389°. δ_H($CDCl_3$, 400 MHz) 1.24 (s, 9H), 1.30 (s, 9H), 1.37 (m, 8H), 1.65 (m, 10H), 1.91 (m, 6H), 3.09 (ddd, J = 8.8, 8.8, 2.4 Hz, 3H), 3.45 (ddd, J = 8.5, 8.5, 3.6 Hz, 3H), 4.05 (ddd, J = 9.9, 9.9, 2.2 Hz, 3H), 4.17 (ddd, J = 10.5, 5.1, 5.1 Hz, 3H), 4.70 (ddd, J = 10.2, 10.2, 3.4 Hz, 3H), 4.79 (ddd, J = 10.9, 6.5, 3 Hz, 3H). δ_C($CDCl_3$, 100 MHz) 25.25, 25.55, 27.10, 27.22, 28.30, 29.50, 54.18, 66.48, 66.90, 70.50, 71.12, 80.17, 80.36, 108.22, 140.96, 141.98, 142.43, 143.65, 143.77, 144.22, 144.60, 145.68, 145.77, 146.35, 146.38, 146.50, 146.59, 146.68, 147.79, 162.39, 162.92. UV/Vis ($CHCl_3$): λ_{max}/nm (ε/$dm^3mol^{-1}cm^{-1}$) 251 (54 250), 281 (47 380), 303 (39 480, sh), 380 (4480), 484 (4150), 563 (1220). CD ($CHCl_3$): 254 nm ($\Delta\varepsilon$ = +28.8), 290 (−9.4), 301.4 (+5.5), 311.2 (−7.7), 329 (+4.8), 356.6 (−8.5), 379.6 (+5.1), 385.2 (+4.2), 394.8 (+6.4), 453.2 (+3.9),

469.6 (+3.0), 488 (+4.7), 515.6 (−1.8), 560.8 (−8.6). MS (FAB, NBA), *m/z*: 1574 ([M^+ + 1], 66%), 720 ([C_{60}^+], 100%).