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A Supramolecular Array of Fullerenes by Quadruple Hydrogen Bonding

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Angew. Chem.

Diethyl-4-oxopimelate-p-tosylhydrazone (2). A solution of diethyl-4-oxopimelate (4.6 g, 20 mmol) and p-toluensulphonylhydrazide (4.32 g, 24 mmol) in ethanol (200 mL) was heated under reflux overnight, and subsequently the reaction mixture was allowed to reach room temperature. After removal of the solvent in vacuo, final purification was done by column chromatography (silica gel; CH₂Cl₂), yielding the pure product as a white crystalline solid (6.81 g, 17 mmol, 85 %); mp 88 - 89 °C; ¹H NMR (CDCl₃, 300 MHz) δ 9.32 (1H, s), 7.83 (2H, d, J = 8.1), 7.26 (2H, d, J = 8.1), 4.07 (2H, q, J = 7.2), 3.98 (2H, q, J = 7.2), 2.61 - 2.38 (8H, m), 2.40 (3H, s), 1.20 (3H, t, J = 7.2), 1.19 (3H, t, J = 7.2); ¹³C NMR (CDCl₃, 75 MHz) δ 174.0, 172.6, 157.1, 143.2, 135.6, 129.0, 128.2, 61.5, 60.3, 30.2, 30.0, 29.6, 24.8, 21.5, 14.0, 13.9; FTIR (KBr, cm⁻¹) 3122 (br), 2992, 2926, 1733, 1703, 1476, 1431, 1409, 1378, 1335, 1314, 1256, 1212, 1187, 1048, 1021, 918, 817, 733, 707, 656, 590, 553; Anal. Calcd. for C₁₈H₂₆N₂O₆S: C: 54.26 %, H: 6.58 %, N: 7.03 %, S:
8.05 %. Found: C: 54.23 %, H: 6.41 %, N: 7.01 %, S: 8.11 %; HRMS (EI+) Calcd. For $^{12}$C$_{18}$H$_{26}$N$_2$O$_6$S: 398.1511. Found: 398.1506.

**Synthesis of methanofullerene diester (3b).** A mixture of diethyl-4-oxopimelate-p-tosylhydrazone (2) (1.86 g, 5 mmol), MeONa (0.265 g, 4.9 mmol) and pyridine (160 mL, anhydrous) was stirred under nitrogen atmosphere during 20 min. After that, a solution of [60]fullerene (1.8 g, 2.5 mmol) in ODCB (250 mL) was added. The resulting solution was heated at 100 ºC overnight. Then, the solvent was removed in vacuo and a mixture of fulleroid 3a and methanofullerene 3b was obtained by column chromatography (silica gel; toluene). In order to convert 3a in 3b the obtained mixture was redissolved in ODCB and irradiated with a sodium flood lamp (500 W) overnight. HPLC analysis showed complete conversion of 3a in 3b. The ODCB was removed in vacuo and the compound was further precipitated and centrifugated using pentane, diethyl ether and methanol, and dried overnight at ~ 50 ºC in vacuo, giving pure 3b (1.16g, 1.24 mmol, 49 %) as a brown solid; mp 217.8 - 218.9 ºC; $^1$H NMR (CDCl$_3$, 300 MHz) δ 4.25 (q, $J = 7.2$, 4H), 3.00 (s, 8H), 1.34 (t, $J = 7.2$, 6H); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 174.4, 147.5, 145.4, 145.2, 145.1, 144.8, 144.7, 144.4, 144.2, 143.6, 143.1, 143.0, 142.9, 142.2, 142.1, 140.9, 137.7, 80.3, 61.0, 42.8, 31.7, 23.5, 14.2; FTIR (KBr, cm$^{-1}$) 2992, 2926, 1732, 1449, 1426, 1373, 1290, 1250, 1183, 1022, 525; UV-Vis (toluene, $\lambda$, (log $\varepsilon$)): 331 (4.67) and 433 nm; MALDI-TOF MS: Calcd for 12C$_71$H$_{18}$O$_4$ (M-): m/z = 934.1. Found: m/z = 934.9; Anal. Calcd. for C$_{71}$H$_{18}$O$_4$: C: 91.21 %, H: 1.94 %. Found: C: 90.22 %, H: 2.09 %.[1]

**Synthesis of methanofullerene dicarboxylic acid (4).** A mixture of diester 3 (0.86 g, 0.92 mmol) in ODCB (180 mL), acetic acid (90 mL), and HCl (37 mL) was heated under reflux overnight. After cooling the reaction mixture to room temperature, the reaction mixture was washed with water (3 x 100 mL) and the organic layer was collected. The solvent was removed in vacuo and the residue was precipitated and centrifugated with pentane, diethyl ether and methanol and dried overnight at ~ 50 ºC in vacuo (see before). The obtained product (4, 0.67 g, 0.76 mmol, 83 %) was used without any further purification in the subsequent step.; mp > 250 ºC; $^1$H NMR (DMSO-d$_6$, 500 MHz) δ 12.44 (s, 2H), 2.90 (br s, 8H); $^{13}$C NMR (DMSO-d$_6$, 125 MHz, 70 ºC) δ 173.0, 147.9, 145.1, 144.3, 144.2, 144.1, 143.8, 143.5, 143.2, 142.8, 142.3, 142.2, 141.4, 141.3, 139.8, 136.7, 81.0, 43.7, 30.8, 23.0; FTIR (KBr, cm$^{-1}$) 3461 (br), 1706, 1444, 1426, 1410, 1295, 1208, 1186, 905, 525; UV-Vis (DMSO, $\lambda$, (log $\varepsilon$)): 331 (4.67), 435 (3.59), 497 (3.43) and 696 nm (3.14); Anal. Calcd. for C$_{67}$H$_{10}$O$_4$: C: 91.21 %, H: 1.94 %. Found: C: 90.22 %, H: 2.09 %.[1]

**Synthesis quadruple hydrogen bonding fullerene derivative 8.** A suspension of dicarboxylic acid 4 (100 mg, 0.112 mmol) in SOCl$_2$ (10 mL) was heated under reflux for 1h. Subsequently, the remaining SOCl$_2$ was removed in vacuo. The remaining solid was redissolved in ODCB (10 mL) and this mixture was heated at 75 ºC for 10 min. A solution of sodium azide (35 mg, 0.55 mmol) in N,N-dimethyl acetamide (10 mL) was added. The resulting mixture was stirred at 75 ºC, and progress was monitored by TLC (silica gel; chloroform) until maximum conversion. Subsequently, 2-amino-4-hydroxy-6-tridecylpyrimidine (129 mg, 0.44 mmol) and anhydrous pyridine (10 mL) were added and the reaction mixture was heated at 100 ºC overnight. After cooling to room temperature the mixture was washed with dilute HCl (3 x 100 mL) and water (2 x 100 mL), and concentrated in vacuo. Column chromatography (silica gel; chloroform : methanol = 99 : 1) gave 8 which was suspended in and centrifuged from subsequently toluene, ether and
methanol giving pure 8 (70 mg, 0.048 mmol, 43 %) as a brown powder; mp 204.7 - 205.7 ºC; 1H NMR (CDCl3/TFA-d1, 500 MHz) δ 11.33 (br s, 6H), 6.23 (s, 2H), 4.06 (d, J = 6.5, 4H), 3.07 (t, J = 6.5, 4H), 2.63 (t, J = 6.5, 4H), 1.66 (m, 4H), 1.35 (m, 4H), 0.89 (t, J = 7.2, 6H); 13C NMR (CDCl3, 125 MHz) δ 172.87, 156.63, 154.10, 152.33, 148.76, 145.42, 145.11, 144.94, 144.64, 144.54, 144.37, 143.67, 143.03, 142.86, 142.64, 142.03, 141.85, 141.85, 140.10, 137.55, 105.87, 78.21, 39.92, 37.74, 32.74, 31.98, 31.85, 31.68, 31.33, 31.17, 29.74, 29.56, 29.43, 29.35, 28.95, 27.28, 26.67, 22.76, 14.22; FTIR (KBr, cm⁻¹) 3213, 3148, 2922, 2850, 1697, 1656, 1585, 1524, 1462, 1306, 1251, 847, 797, 766, 526; UV-Vis (CHCl3, λ (log ε)): 328 (4.45), 432 (4.27), 492 (3.96), and 698 nm (3.11); MALDI-TOF MS: Calcd for 12C_{101}H_{70}N_{8}O_{4} (M⁻): m/z = 1458.6. Found: m/z = 1457.8; Anal. Calcd. for C_{101}H_{70}N_{8}O_{4}: C: 83.11 %, H: 4.83 %, N: 7.68 %. Found: C: 82.06 %, H: 4.42 %, N: 7.11 %.[1]

[1] It is known that the insoluble derivatives of C_{60} give a very low percent of carbon (see for instance: R. Gonzalez, J.C. Hummelen, F. Wudl J. Org. Chem. 1995, 60, 2618).