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A Supramolecular Array of Fullerenes by Quadruple Hydrogen Bonding

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Angew. Chem.

General remarks.

All reagents and solvents were used as received or purified using standard procedures. [60]Fullerene (99.5%) was purchased from Southern Chemical Group, LLC and used without purification. All reactions were performed under a nitrogen atmosphere unless indicated otherwise. Flash chromatography was performed using Kieselgel Merck Type 9385 (230-400 mesh). Analytical thin layer chromatography (TLC) was performed using aluminum coated Merck Kieselgel 60 F₂₅₄ plates. Melting points were determined with a Mettler FP1 melting point apparatus equipped with a Mettler FP2 microscope. ¹H-NMR and ¹³C-NMR spectroscopy were performed on a Varian Unity Plus (500 MHz) instrument or on a Varian VXR-300 (300 MHz) instrument as indicated, at 298 K. Coupling constants (*J*) are denoted in Hz. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = double doublet, m = multiplet, br = broad. FT-IR spectra were recorded on a Mattson Galaxy 4020 instrument. UV-Vis spectra were recorded on a Hewlett Packard HP 8452 UV-Vis spectrophotometer. High Resolution Mass Spectroscopy (HRMS) were performed on a JEOL JMS 600 spectrometer (positive ion EI mode). MALDI-TOF-MS measurements were performed on a Micromass ToFSpec E® apparatus (negative-ion reflector mode) by using elemental sulfur as a matrix (See: Brune, D. C. *Rapid Commun. Mass Spectrom.* 1999, 13, 384 - 389). Measurements were performed on aliquots of the analyte (1 mg/mL) and elemental sulfur (10 mg/mL) in CS₂ or CHCl₃. HPLC analyses were performed on a Hewlett Packard HP LC-Chemstation 3D (HP 1100 Series) using an analytical Cosmosil Buckyprep® column (4.6 x 250 mm). Cyclic Voltammetry was performed using an Autolab PGStat 100. Elemental analysis were performed by the Microanalytical Department of this laboratory.

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 (6.81g, 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 $^{12}\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_6\text{S}$: 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 °C 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 °C *in vacuo*, giving pure **3b** (1.16g, 1.24 mmol, 49 %) as a brown solid; mp 217.8 - 218.9 °C; ^1H 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, λ , (log ϵ)): 331 (4.67) and 433 nm (3.54); MALDI-TOF MS: Calcd for $^{12}\text{C}_{71}\text{H}_{18}\text{O}_4$ (M): m/z = 934.1. Found: m/z = 934.9; Anal. Calcd. for $\text{C}_{71}\text{H}_{18}\text{O}_4$: 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 °C *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 °C; ^1H NMR ($\text{DMSO}-d_6$, 500 MHz) δ 12.44 (s, 2H), 2.90 (br s, 8H); ^{13}C NMR ($\text{DMSO}-d_6$, 125 MHz, 70 °C) 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, 142.1, 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 , λ (log ϵ)) 331 (4.67), 435 (3.59), 497 (3.43) and 696 nm (3.14); Anal. Calcd. for $\text{C}_{67}\text{H}_{10}\text{O}_4$: C: 91.57 %, H: 1.15 %. Found: C: 90.97 %, H: 1.48 %.^[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 °C 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 °C, 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 to 100 °C 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 °C; ¹H NMR (CDCl₃/TFA-*d*₁, 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, 44H), 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, 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 ¹²C₁₀₁H₇₀N₈O₄ (M⁺): *m/z* = 1458.6. Found: *m/z* = 1457.8; Anal. Calcd. for C₁₀₁H₇₀N₈O₄: 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 C₆₀ give a very low percent of carbon (see for instance: R. Gonzalez, J.C. Hummelen, F. Wudl *J. Org. Chem.* **1995**, *60*, 2618).