

Supplementary Data

A chiral dumbbell shaped bis(fullerene) oligoelectrolyte

Nikos Chronakis,^{*a} Uwe Hartnagel,^b Martin Braun^b and Andreas Hirsch^{*b}

^a Department of Chemistry, University of Cyprus, P. O. Box 20537, 1678 Nicosia, Cyprus. Fax: (+357) 22892801; Tel: (+357) 22892781; E-mail: nchronak@ucy.ac.cy

^b Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestrasse 42, 91054 Erlangen, Germany. Fax: (+49) 9131 8526864; Tel: (+49) 9131 8522537; E-mail: andreas.hirsch@chemie.uni-erlangen.de

Abbreviations

ODCB	<i>ortho</i> -Dichlorobenzene
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
NBA	3-Nitrobenzyl alcohol
DMA	9,10-Dimethylantracene
ATR	Attenuated Total Reflection
Phosphazene baseP ₁ - <i>t</i> -Bu	<i>tert</i> -Butylimino-tris(dimethylamino)phosphorane

Experimental Part

Bis(fullerene) (5)

Bis-[60]fullerenyl-cyclo-[2]-octylmalonate

Cyclo-[2]-octylmalonate **4** (30 mg, 70 μmol, 1 equiv) and C₆₀ (252 mg, 0.35 mmol, 5 equiv) were dissolved in ODCB (15 mL) under argon atmosphere. A standard solution of iodine in ODCB (10 mg/mL) was prepared and 2 equiv (36 mg, 3.6 mL standard solution) were added. DBU (58 μL, 5 equiv) was diluted in ODCB (5 mL) and added dropwise over a period of 2 h. After stirring for 6 h the solution was directly chromatographed on SiO₂ by using toluene as an eluent. Repeated preparative TLC with toluene (SiO₂, R_f(C₆₀) = 0.9, R_f(**5**) = 0.7) yielded a red-wine coloured solution which was evaporated and dried *in vacuo*. Due to the poor solubility of **5**, yield losses

during purification were inevitable. The brown solid (14 mg, 11 %) is soluble e.g. in CS₂ and ODCB. ¹H NMR (CDCl₃/CS₂ = 80/20, 400 MHz, RT): δ = 4.47 (t, ³J = 6.6 Hz, 8H), 1.96-1.89 (m, 8H), 1.61-1.54 (m, 16H). ¹³C NMR (CDCl₃/CS₂ = 80/20, 100.5 MHz, RT): δ = 162.4 (4C, C=O), [144.9, 144.8, 144.8, 144.5, 144.3, 144.3, 143.5, 142.8, 142.7, 142.7, 141.9, 141.5, 140.6, 138.8 (sp² fullerene)], 71.2 (4C, sp³ fullerene), 66.8 (4C, -O-CH₂-), 51.6 (2C, bridgehead sp³ C), 29.59 (2C), 28.75 (2C), 26.14 (4C). UV/Vis (CH₂Cl₂/ODCB = /): λ_{max} = 326, 425, 489 nm. MS (FAB, NBA): *m/z* = 1865 [M⁺], 720 [C₆₀⁺]; MW = 1865.77 g/mol.

Boc-protected malonate **9**

In a dry 1 L round-bottomed flask equipped with a gas inlet, 100 mL dropping funnel, and magnetic stirrer, N-Boc-aminoethanol (5.00 g, 31.02 mmol, 2.2 equiv) was dissolved under nitrogen in dry dichloromethane (300 mL). Pyridine (1.71 mL, 21.17 mmol, 1.5 equiv) was added to the solution and the reaction mixture was cooled in an ice bath. Subsequently, a solution of malonyl dichloride (1.37 ml, 14.12 mmol, 1.0 equiv) in dry dichloromethane (100 mL) was added dropwise over a period of 1 hour. The reaction mixture was stirred for additionally 2 hours at 0 °C followed by stirring at room temperature overnight. After extracting with a saturated solution of NH₄Cl twice and finally with water followed by drying over MgSO₄, filtrating and concentrating, purification was performed by flash chromatography on silica gel using a mixture of hexane/EtOAc = 60:40 as eluent. Finally the product fractions were evaporated in vacuum to isolate **9** as a colorless oil (3.97 g, yield 72 %). ¹H-NMR (CDCl₃, 400 MHz, RT): δ = 4.95 (br, 2H, NH), 4.18 (t, ³J = 5.2 Hz, 4H, OCH₂), 3.38 (m, 4H, CH₂NH), 3.36 (s, 2H, O₂CCH₂CO₂), 1.40 (s, 18H, C(CH₃)₃) ppm. ¹³C-NMR (CDCl₃, 100.5 MHz, RT): δ = 166.46 (2C, C=O), 155.86 (2C, CONH), 79.60 (2C, C(CH₃)₃), 64.74 (2C, OCH₂), 41.21 (1C, O₂CCH₂CO₂), 39.34 (2C, CH₂NH), 28.24 (6C, C(CH₃)₃) ppm. MS (FAB, NBA): *m/z* = 391 [M]⁺; MW = 390.43 g/mol. C₁₇H₃₀N₂O₈: calcd: C 52.30, H 7.74, N 7.18; found: C 52.41, H 7.80, N 7.20.

Bis(fullerene) *ent*-**8**

In a dry 1000 mL two-necked flask equipped with gas inlet and dropping funnel, C₆₀ (432 mg, 0.60 mmoles, 2 equiv) was dissolved in dry toluene (450 mL). Subsequently, the bismalonate (+)-**7** (138 mg, 0.30 mmoles, 1 equiv) and iodine

(167.6 mg, 0.66 mmol, 2.2 equiv) were added to the solution followed by the dropwise addition of a solution of DBU (232.7 μ L, 1.56 mmol, 5.2 equiv) in dry toluene (50 mL) over a period of 30 min. The reaction mixture was stirred overnight at RT and the raw mixture was chromatographed on SiO₂. Elution with toluene afforded the unreacted C₆₀ and then, the eluent was changed to toluene/EtOAc = 90:10 to elute a red-wine coloured fraction. After evaporation of the solvent and precipitation from CHCl₃ by addition of pentane, the bis(fullerene) *ent*-**8** was isolated as a brown powder (150 mg, yield 26%). ¹H-NMR (CDCl₃/CS₂ = 80/20, 300 MHz, RT): δ = 1.49 (s, 12H, CH₃-C-CH₃), 4.44 (br s, 4H, methine H), 4.71 (m, 8H, methylene H) ppm. ¹³C-NMR (CDCl₃/CS₂ = 80/20, 100.5 MHz, RT): δ = 26.93 (4C, CH₃-C-CH₃), 50.87 (2C, bridgehead sp³ C), 66.35 (4C, methylene C), 71.03 (4C, sp³ fullerene C), 76.68 (4C, methine C), 110.89 (2C, CH₃-C-CH₃), [139.21, 140.90, 141.70, 142.08, 142.89, 142.92, 142.96, 143.77, 144.44, 144.56, 144.59, 144.86, 145.07, 145.18 (sp² fullerene)], 162.63 (4C, C=O) ppm. MS (FAB, NBA), *m/z*: 1898 [M⁺]; MW = 1897.68 g/mol.

Bis(fullerene) *ent*-10

Bis(fullerene) *ent*-**10** was synthesized by a DMA template mediated cyclopropanation reaction.

References:

- a) I. Lamparth, C. Maichle-Moessmer, A. Hirsch, *Angew. Chem. Int. Ed.* **1995**, *34*, 1607; *Angew. Chem.* **1995**, *107*, 1755.
- b) I. Lamparth, A. Herzog, A. Hirsch, *Tetrahedron* **1996**, *52*, 5065.
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In a dry 100 mL two-necked flask equipped with gas inlet and dropping funnel, bis(fullerene) *ent*-**8** (60 mg, 31.6 μ mol, 1.0 equiv) was dissolved in the presence of DMA (131 mg 633 μ mol, 20.0 equiv) under nitrogen in dry dichloromethane (40 mL). The solution was stirred for 2 hours under exclusion of light followed by the addition of malonate **9** (247 mg, 633 μ mol, 20.0 equiv) and CBr₄ (210 mg, 633 μ mol, 20 equiv). After stirring for a few minutes to allow complete dissolution, phosphazene base P₁-*t*-Bu (247 μ L, 949 μ mol, 30 equiv) was diluted in 20 mL dry dichloromethane and added dropwise over a period of one hour. The reaction mixture was stirred for

two days at room temperature in the dark until TLC control remained unchanged. After extracting with a saturated NH_4Cl solution twice and water to neutralize the strong base followed by drying over MgSO_4 , filtrating and concentrating, purification was achieved by repeated flash chromatography on silica gel using a gradient ($\text{CH}_2\text{Cl}_2/\text{EtOAc}$ 80:20→50:50). The product fractions were evaporated and repeatedly precipitated from CH_2Cl_2 by adding pentane, centrifuged and dried in vacuum. 69 mg of the pure product *ent-10* was obtained as a pale orange powder (69 mg, 12.0 μmol , yield 38 %). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, RT): δ = 5.16 (br, 20H, NH), 4.32 (br, 40H+8H+4H, OCH_2 , OCH_2 , OCH), 3.45 (br, 40H, CH_2NH), 1.42 (s, 112H, $\text{C}(\text{CH}_3)_3$) ppm. $^{13}\text{C-NMR}$ (CDCl_3 , 100.5 MHz, RT): δ = 163.59 (24C, C=O), 155.90 (20C, CONH), 46.03, 141.04 (96C, $\text{sp}^2\text{-C}$), 110.97 (2C, $\text{C}(\text{CH}_3)_2$), 79.75 (20C, $\text{C}(\text{CH}_3)_3$), 68.89 (20C, $\text{sp}^3\text{-C}$), 68.09 (4C, $\text{sp}^3\text{-C}$), 66.03 (24C, OCH_2), 44.82 (12C, O_2CCCO_2), 39.34 (20C, CH_2NH), 28.31 (60C, $\text{C}(\text{CH}_3)_3$), 26.89 (4C, $\text{C}(\text{CH}_3)_2$) ppm. MS (FAB, NBA): m/z = 5912 $[\text{M}+\text{Cs}]^+$, 5804 $[\text{M}+\text{Na}]^+$, 5781 $[\text{M}]^+$; MW = 5782.73 g/mol. IR (ATR): ν_{max} = 3362, 2980, 2934, 1749, 1702, 1517, 1455, 1393, 1366, 1247, 1216, 1166, 1038, 865, 733, 714 cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} = 243, 277 (br), 318, 333 nm.

Bis(fullerene) *ent-11*

Trifluoroacetic acid (2.0 mL, 26.0 mmol) was added to a solution of bis(fullerene) *ent-10* (50 mg, 8.6 μmol) in dichloromethane (25 mL) and stirred for 12 h at room temperature. The reaction mixture was concentrated, repeatedly co-evaporated with methanol and finally dried in vacuum to afford the product *ent-11* in almost quantitative yield (99 %, 51 mg, 8.5 μmol) as a pale-orange powder. $^1\text{H-NMR}$ (MeOD-d_3 , 400 MHz, RT): δ = 4.49 (br, 40H+8H+4H, OCH_2 , OCH_2 , OCH), 3.29 (br, 40H, CH_2NH) ppm. $^{13}\text{C-NMR}$ (MeOD-d_3 , 100.5 MHz, RT): δ = 164.56 (24C, C=O), 147.70, 142.54 (96C, $\text{sp}^2\text{-C}$), 70.25 (24C, $\text{sp}^3\text{-C}$), 65.04 (20C, OCH_2), 42.76 (12C, O_2CCCO_2), 39.79 (20C, CH_2NH) ppm. IR (ATR): ν_{max} = 3360, 2980, 2934, 1751, 1702, 1517, 1458, 1370, 1366, 1247, 1216, 1160, 1038, 865, 733, 698 cm^{-1} . UV/Vis (CH_2Cl_2): λ_{max} = 245, 279, 336 nm.

Calculations

The MM+ and PM3 calculations as well as the MD simulations were done with HyperChem (Hyperchem 7.5, Copyright 2004, Hypercube Inc., <http://www.hyper.com>) The MD-simulation parameters were:

Heat time: 15 ps

Run time: 15 ps

Cool time: 15 ps

Step size: 1 fs

Starting temp.: 0 K

Simulation temp.: 370 K

Final temp.: 0 K

Temp. step: 0.2 K