Reverse shuttling in a fullerene stoppered rotaxane

Aurelio Mateo-Alonso,^{*,‡} Giulia Fioravanti,[†] Massimo Marcaccio,[†] Francesco Paolucci,^{*,†} Dhiredj C. Jagesar,[§] Albert M. Brouwer,[§] and Maurizio Prato.^{*,‡}

[‡]Dipartimento di Scienze Farmaceutiche, Università degli Studi di Trieste, Piazzale Europa 1, 34127 Trieste, Italy. [†]Dipartimento di Chimica "G. Ciamician", Università di Bologna, v. Selmi 2, 40126 Bologna, Italy. [§]Van 't Hoff Institute for Molecular Sciences, Faculty of Science, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands.

Email: amateo@units.it, prato@units.it, francesco.paolucci@unibo.it

Supporting information.

NMR spectra were recorded on a Varian Gemini-200 (200 MHz) or on a Jeol (400 MHz) at room temperature. Chemical shifts reported in ppm are referred to TMS. Signals on thread **6** and rotaxane **7** were assigned by COSY experiments.

Infrared spectra were recorded on a Jasco FTIR-200 spectrometer.

Mass Spectroscopy: Electrospray (ES-MS) experiments were recorded at Università degli Studi di Trieste on a Perkin-Elmer API1 at 5600 eV.

UV-Vis-NIR measurements were recorded on a Varian 5000 UV-Vis-NIR spectrometer.

Commercial compounds were used as received.

EDC (*N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride), HOBt (1-Hydroxybenzotriazole hydrate), DCM (dichloromethane), TFA (trifluoroacetic acid), DMAP (4-Dimethylaminopyridine).

Scheme S1

Synthesis of 3

EDC (2.40 g, 10 mmol) was added in small portions to a solution of 11-Boc-aminoundecanoic acid (2.5 g, 6.6 mmol), 2,2'-diphenylethylamine (2.465 g, 10 mmol), HOBt (1.69 g, 10 mmol) in DCM (200 mL). The resulting solution was stirred at room temperature for 24 h. The solution was taken up with DCM and was washed with aqueous HCl (1M, $\times 2$), aqueous NaOH (1M) and with brine. The organic phase was dried over magnesium sulfate and the solvent was evaporated yielding the title compound (3.73 g, 94%).

^1H NMR (200 MHz, CDCl_3): 7.5-7.1 (m, 10H, Ph); 5.72 (s, 1H, NH); 4.68 (s, 1H, NH); 4.22 (t, 1H, $J=7.83$ Hz; CHPh_2); 3.87 (dd, 2H, $J=5.73$ and 7.79 Hz; CH_2CHPh_2); 3.10 (c, 2H, $J=6.70$ Hz, BocNHCH_2); 2.04 (t, 2H, $J=7.26$ Hz, CH_2CONH); 1.45 (s, 9H, Boc); 1.3-1.0 (m, 16H).

^{13}C NMR (50 MHz, CDCl_3): 172.91; 155.78; 141.71; 128.43; 127.82; 126.52; 78.72; 50.41; 43.57; 40.47; 36.53; 29.92; 29.33; 29.20; 29.15; 29.12; 28.98; 28.32; 26.65; 25.55.

MS (m/z): 504 ($\text{M}^+ + \text{Na}$)

Synthesis of 4

3 (3.24 g, 6.74 mmol) was stirred at room temperature in DCM (50 mL) and TFA (10 mL) for 18 h. The solvent was evaporated under vacuum and the residue was dissolved in DCM and washed with aqueous NaOH (1M, $\times 2$) and brine. The organic phase was dried over magnesium sulfate and the solvent was eliminated under vacuum. The residue was dissolved in THF (anhydrous, 40 mL) under argon. Succinic anhydride (1.34 g, 7.77 mmol) and DMAP (95 mg, 0.77 mmol) were added and the mixture was stirred at room temperature for 18 hours. The solution was taken up with ethyl acetate and was washed with aqueous HCl (1M, $\times 2$) and brine. The organic phase was dried over magnesium sulfate and the solvent was evaporated yielding the title compound (2.22 g, 69%).

^1H NMR (200 MHz, CDCl_3): 7.5-7.2 (m, 10H, Ph); 6.50 (t, 1H, $J=5.5$ Hz, NH); 5.74 (t, 1H, $J=5.4$ Hz, NH); 4.21 (t, 1H, $J=7.7$ Hz, CHPh_2); 3.90 (dd, 2H, $J=5.8$ and 7.7 Hz, CH_2CHPh_2); 3.24 (c, 2H, $J=6.19$ Hz, $\text{CONHCH}_2\text{CH}_2$); 2.7-2.4 (m, 4H, succinic); 2.08 (t, 2H, $J=7.20$ Hz, CH_2CONH); 1.7-1.0 (m, 14H).

^{13}C NMR (50 MHz, CDCl_3): 175.39; 173.65; 172.48; 141.69; 128.59; 127.91; 126.72; 125.37; 50.47; 43.79; 39.72; 36.59; 30.87; 30.30; 30.09; 29.66; 29.26; 29.16; 29.00; 26.87; 26.63; 25.52.

MS: 481 (M^+H).

IR (NaCl): 3315; 2923; 2850; 1694; 1641; 1543; 1493; 1427; 1260; 1221; 1194; 1096; 1032; 801; 755; 737; 699.

Synthesis of 6

A solution of acid **4** (266 mg, 0.554 mmol), EDC (120 mg, 0.609 mmol), HOBT (82 mg, 0.609 mmol) in DCM was stirred at room temperature for 15 min. Then, it was added to a solution of building block **5**¹ (260 mg, 0.277 mmol) in pyridine (26 ml). The resulting solution was stirred for 1 h. Then it was taken up with chloroform and washed with aqueous HCl (1M, $\times 3$) and brine. The organic phase was dried over magnesium sulfate and the solvent was evaporated under vacuum. The thread was purified by flash chromatography (CHCl_3 :MeOH 98:2) to yield thread **6** (242 mg, 69%).

^1H NMR (400 MHz, CDCl_3): 7.35-7.15 (m, 10H, Ph); 6.79 (t, 1H, $J=5.07$ Hz, A); 5.93 (t, 1H, $J=4.30$ Hz, B); 5.35 (t, 1H, $J=5.44$ Hz, C); 4.46 (s, 4H, D); 4.17 (t, 1H, $J=8.00$ Hz, E); 3.88 (dd, 2H, $J=5.84$ and 7.96 Hz, F); 3.79 (c, 2H, $J=5.73$ Hz, G); 3.27 (t, 2H, $J=6.09$ Hz, I); 3.22 (c, 2H, $J=6.17$ Hz, J); 2.70-2.55 (m, 4H, K); 2.04 (t, 2H, $J=7.70$ Hz, L); 1.52-1.15 (m, 16H).

^1H NMR (400 MHz, $\text{DMSO}-d_6$): 8.17 (t, 1H, $J=5.31$ Hz, A); 7.80 (t, 2H, $J=4.80$ Hz, B+C); 7.35-7.12 (m, 10H, Ph); 4.51 (s, 4H, D); 4.18 (t, 2H, $J=8.02$ Hz, E); 3.66 (dd, 2H, $J=6.23$ and 7.61 Hz, F); 3.60 (c, 2H, $J=7.21$ Hz, G); 3.17 (t, 2H, $J=6.54$ Hz, J); 3.01 (t, 2H, $J=6.84$ Hz, I); 2.45-2.30 (m, 4H, K); 1.92 (t, 2H, $J=7.11$ Hz, L); 1.42-1.00 (m, 16H).

MS: 1269 (M^+H).

IR (NaCl): 3052; 3000; 2918; 2848; 1718; 1635; 1539; 1491; 1451; 1374; 1260; 1183; 1119; 767; 750; 700.

Synthesis of rotaxane **7**

A solution of p-xylylenediamine (390 mg, 2.865 mmol) in chloroform (anhydrous stabilized with amylenes, 40 mL) and a separate solution of isophthaloyl chloride (582 mg, 2.865 mmol) in chloroform (anhydrous stabilized with amylenes, 40 mL) were added dropwise, simultaneously for 4 hours to a stirred solution of the thread number **6** (242 mg, 0.191 mmol) and containing NEt₃ (1 mL, 5.8 mmol) in CHCl₃ (anhydrous stabilized with amylenes, 125 mL) under argon. After the addition the reaction mixture was stirred overnight at room temperature. The solution was filtered through celite, concentrated to dryness. The rotaxane **7** (27 mg, 8%) was separated from the unreacted thread by chromatography (CHCl₃:MeOH 99.5:0.5 (thread) $\Rightarrow$ CHCl₃:MeOH 99:1 (rotaxane)) followed by reprecipitation (DCM/diethyl ether, $\times 3$).

¹H NMR (400MHz, CDCl₃): 8.47 (s, 2H, a); 8.18 (dd, 4H, J=1.25 Hz and 7.82 Hz, b); 7.65 (t, 4H, J=5.24 Hz, c); 7.58 (t, 2H, J=7.70 Hz, d); 7.35-7.20 (m, 10H, Ph); 7.21 (s, 8H, e); 6.52 (m, 1H, A); 5.92 (m, 1H, B); 5.60 (m, 1H, C); 4.55 (d, 8H, J=5.13 Hz, f); 4.42 (s, 4H, D); 4.16 (t, 1H, J=8.01 Hz, E); 3.82 (dd, 2H, J=5.74 and 8.01 Hz, F); 3.60 (c, 2H, J=5.50 Hz, G); 3.22 (t, 2H, J=6.30 Hz, I); 3.01 (c, 2H, J=5.50 Hz, J); 1.88 (t, 2H, J=7.24 Hz, L); 1.60-1.00 (m, 16H); 0.90-0.80 (m, 4H, K).

¹H NMR (400 MHz, DMSO-*d*₆): 8.75 (t, 4H, J=4.71 Hz, c); 8.34 (s, 2H, a); 8.01 (m, 1H, A); 7.96 (d, 4H, J=7.62 Hz, b); 7.80-7.70 (m, 2H, B+C); 7.48 (t, 2H, J=7.82 Hz, d); 7.30-7.10 (m, 10H, Ph); 7.23 (s, 8H, e); 4.60-4.25 (m, 8H, f); 3.81 (s, 4H, D); 3.65 (t, 1H, J=6.31 Hz, E); 3.03 (m, 2H, G); 2.81 (m, 2H, I); 2.05 (m, 1H, J); 2.10-1.90 (m, 4H, K); 1.78 (t, 2H, J=7.06 Hz, L); 1.30-0.75 (m, 16H).

MS: 1801 (M⁺+H).

IR (NaCl): 3288; 3079; 2921; 2850; 1629; 1544; 1456; 1388; 1190; 748.

Figure S1 ^1H NMR spectrum of **3** in CDCl_3

Figure S2 ^{13}C NMR spectrum of **3** in CDCl_3

Figure S3 ^1H NMR spectrum of **4** in CDCl_3

Figure S4 ^{13}C NMR spectrum of **4** in CDCl_3

Figure S5 ^1H NMR spectrum of thread **6** in CDCl_3

Figure S6 ^1H NMR spectrum of rotaxane **7** in CDCl_3

Figure S7 COSY spectrum of rotaxane **7** in CDCl_3

Figure S8 COSY spectrum of rotaxane **7** in DMSO- d_6

Absorbance

Absorbance spectra were recorded in DMSO, PhCN and DCM. (Cary3 spectrometer, 1cm pathlength) concentrations were ca 2×10^{-5} M. All spectra are scaled to the absorbance maximum between 430 and 440 nm.

Figure S9 Scaled absorbance spectra of thread **6** (····) and rotaxane **7** (—) in (a) CH₂Cl₂, and (b) PhCN.

Figure S10 Scaled absorbance spectra of thread **6** (black) and rotaxane **7** (red) in DMSO.

T-T absorption

Figure S11 T-T absorption spectra of thread **6** (····) and rotaxane **7** (—) in (a) PhCN and (b) DMSO ($\lambda_{\text{exc}} = 435 \text{ nm}$, 4 mJ pulse^{-1}).

Cyclic Voltammetry

The cyclic voltammetry (CV) curve for a 0.5 mM of rotaxane **7** (blue line) in THF at 25°C and 1 V/s (Figure 5) displays three reversible reduction peaks (A, B, and C), with half peak potentials of -0.599 V, -1.127 V, and -1.748 V, respectively, due to reduction of fullerene. The CV response of thread **6** (red dashed line) displays a similar cathodic signal

Figure S12 Voltammetry curves recorded using a Pt working electrode at 1 V s⁻¹ scan rate (THF, TBAPF₆ 0.1 mol L⁻¹). An Ag/Ag⁺ electrode was used as reference electrode.

Bibliography

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