**Supporting Information**

# Macroscopic transport by synthetic molecular machines

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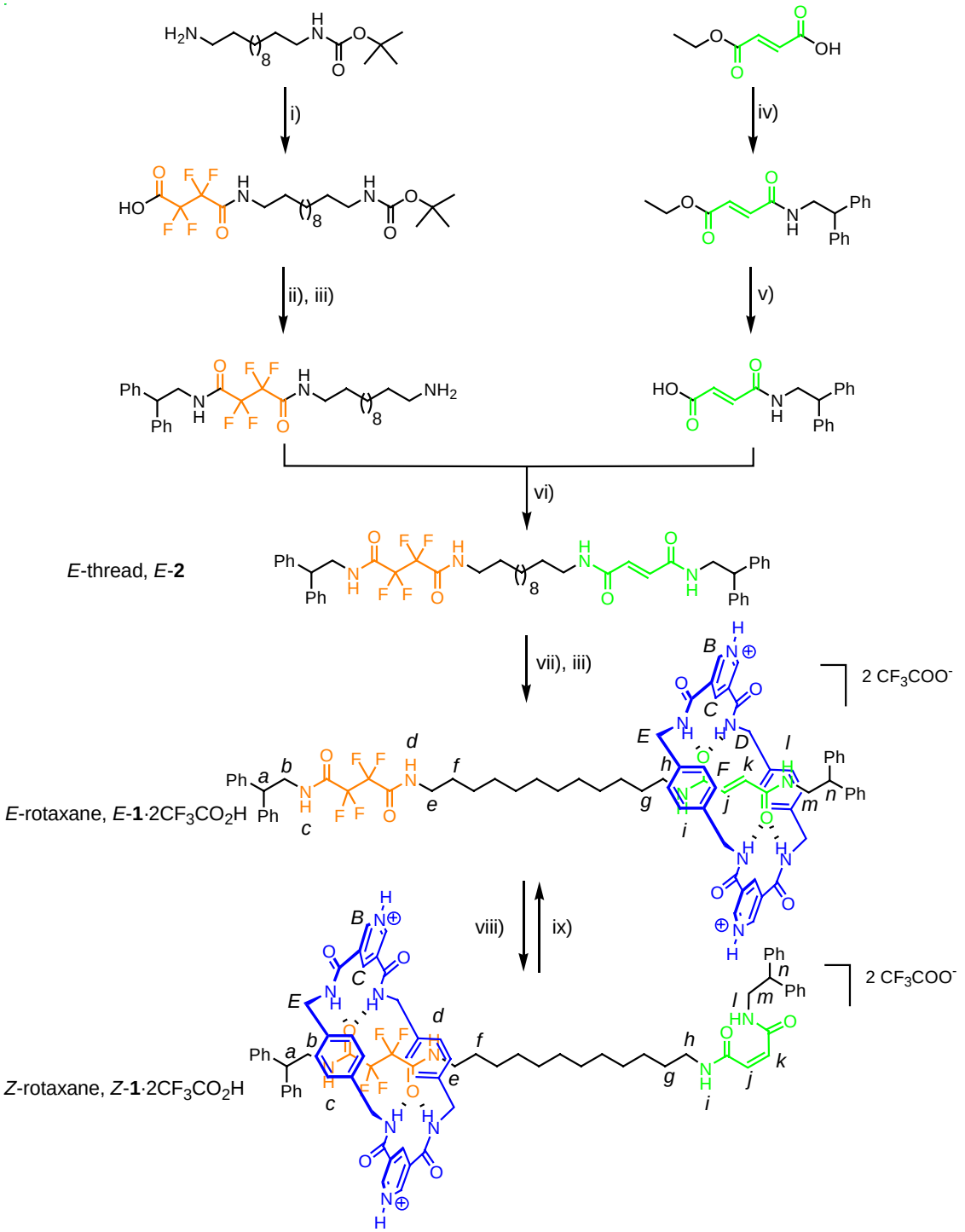
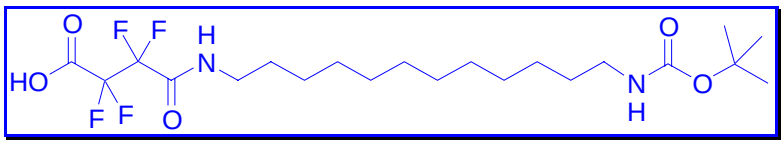



*Reagents and conditions:* (i) perfluorosuccinic anhydride, $Et_3N$, $CH_2Cl_2$, 12 h, 83%; (ii) 2,2-diphenylethylamine, dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (BtOH), $CH_2Cl_2$, 5h, 90%; (iii) trifluoroacetic acid, $CH_2Cl_2$, then 1M NaOH (aq.), 92% (iv) 4-dimethylaminopyridine (DMAP), 1-(3-dimethylaminopropyl)-3-ethyl-carbodiimide hydrochloride (EDCI·HCl), $CH_2Cl_2$, 24 h, 82%; v) 1 M NaOH(aq), EtOH, 16 h, 90%; vi) benzotriazol-1-yloxy-tris(dimethylamino) phosphonium hexafluorophosphate (BOP), $Et_3N$, $CH_2Cl_2$, 5 h,

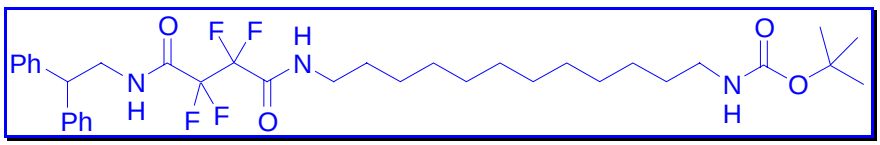
47%; vii) 3,5-pyridinedicarbonyl dichloride, *p*-xylylenediamine, $Et_3N$, $CHCl_3$, 65%; viii) 254 nm, $CH_2Cl_2$, 5 min, 48%; ix) $C_2H_2Cl_4$, 115 °C, 3 days, 90%.

**_N_-(12-*tert*-Butoxycarbonylaminododecyl)-2,2,3,3-tetrafluorosuccinamic acid, S1**



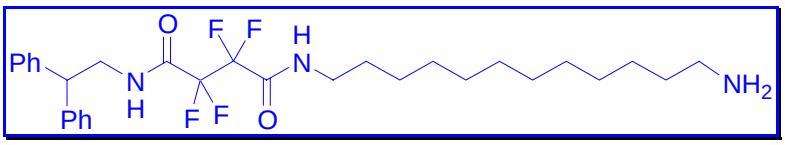

To a stirred solution of 12-aminododecylcarbamic acid tert-butyl ester (prepared as described in A Altieri, G Bottari, F Dehez, D A Leigh, J K Y Wong and F Zerbetto, *Angew. Chem. Int. Ed.* 2003, **42**, 2296-2300) (3.71 g, 12.4 mmol) in $CH_2Cl_2$ (100 mL) was added perfluorosuccinic anhydride (2.13 g, 12.4 mmol). The reaction mixture was allowed to stir at room temperature for 6 h. The solvent was removed under reduced pressure and the resulting solid recrystallized from $CH_2Cl_2$ to obtain **S1** as a colourless solid. 4.86 g (83%); m.p. 113 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ = 12.14 (br s, 1H, COOH), 7.87 (t, $J$ = 8.3 Hz, 1H, $CF_2CONH$), 4.80 (t, $J$ = 5.6 Hz, 1H, $CH_2CONH$), 3.57 (q, $J$ = 6.7 Hz, 2H, $CF_2CONHCH_2$), 3.37 (m, 2H, $CH_2NHCO_2{}^tBu$), 1.87 (m, 2H, $CF_2CONHCH_2CH_2$), 1.79 (br s, 11H, $CH_2CH_2NHCO_2{}^tBu$ + $^tBu$), 1.54 (m, 16H, alkyl chain); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 182.27, 167.69, 157.80, 108.85, 105.89, 43.91, 40.62, 40.01, 30.01, 29.51, 29.45, 29.42, 29.37, 29.20, 29.09, 28.92, 28.43, 26.71; $^{19}$F NMR (235 MHz, $CDCl_3$): δ = -119.92 (t, 2F, $J$ = 4.1 Hz, $CF_2$), -118.00 (br s, 2F, $CF_2$); HRMS calcd. for $C_{21}H_{37}F_4N_2O_5$ [M+H$^+$] 473.26386 found (FAB, 3-NOBA matrix) 473.26792

**_N_-(12-*tert*-Butoxycarbonylaminododecyl)-_N'_-(2,2-diphenylethyl)-2,2,3,3-tetrafluorosuccinamide, S2**



To a stirred solution of *N*-(12-*tert*-butoxycarbonylaminododecyl)-2,2,3,3-tetra fluorosuccinamic acid, **S1** (3.00 g, 6.36 mmol) in anhydrous $CH_2Cl_2$ (40 mL) was added 2,2-diphenylethylamine (1.25 g, 6.36 mmol), DCC (1.96 g, 9.54 mmol) and HOBt (1.29 g, 9.54 mmol) added in this order under argon at 25°C. The solution was allowed to stir for 6 h. The reaction mixture was filtered and concentrated under reduced pressure to afford a yellow oil that was purified by column chromatography ($CH_2Cl_2$/EtOAc) to give **S2** as a colourless solid. 3.73 g (90%); m.p. 121 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.20 (m, 10H, Ph), 6.60 (br s, 2H, NHCOCF$_2$CF$_2$CONH), 4.45 (br s, 1H, CH$_2$CONH), 4.16 (t, 1H, *J* = 8.0 Hz, CH$_2$CHPh$_2$), 3.92 (t, 2H, *J* = 7.0 Hz, CH$_2$CHPh$_2$), 3.24 (q, *J* = 6.7 Hz, 2H, CF$_2$CONHCH$_2$), 3.02 (q, *J* = 6.5 Hz, 2H, CH$_2$NHCO$_2$$^t$Bu), 1.48 (m, 2H, CF$_2$CONHCH$_2$CH$_2$), 1.36 (br s, 11H, CH$_2$CH$_2$NHCO$_2$$^t$Bu + $^t$Bu), 1.18 (m, 16H, alkyl chain); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 158.98 (x2), 157.56, 140.92, 128.87, 127.93, 127.15, 109.32, 105.00, 50.06, 49.73, 44.11 (x2), 40.02, 30.05(x2), 29.43, 29.38, 29.24, 29.09 (x2), 28.92, 28.43, 26.61; $^{19}$F NMR (235 MHz, $CDCl_3$): δ = -120.61 (s, 2F, $CF_2$), -120.82 (s, 2F, $CF_2$); HRMS calcd. for $C_{35}H_{50}F_4N_3O_4$ [M+H$^+$] 652.37374 found (FAB, 3-NOBA matrix) 652.36972

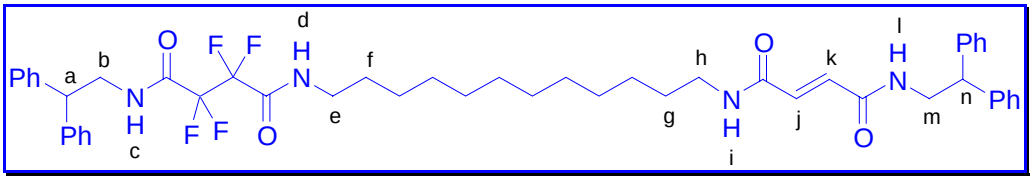
**_N_-(12-aminododecyl)-_N'_-(2,2-diphenylethyl)-2,2,3,3-tetrafluorosuccinamide, S3:**




A solution of *N*-(12-*tert*-butoxycarbonylaminododecyl)-*N'*-(2,2-diphenyl ethyl)-2,2,3,3-tetrafluorosuccinamide, **S2** (1.5 g, 2.30 mmol) in trifluoroacetic acid (TFA, 5 mL) was stirred at rt for 30 minutes. The reaction mixture was concentrated under reduced pressure and $CH_2Cl_2$ (20 mL) added. The organic phase was washed with 1N NaOH (2 x 10 mL), brine (1 x 10 mL), dried over anhydrous $MgSO_4$, filtered and the filtrate concentrated to give the product as a colourless solid. 1.17 g (92%); m.p. 85 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.26 (m, 4H, ArH), 7.18 (m, 6H, ArH), 6.54 (br s, 2H, NHCOCF$_2$CF$_2$CONH), 4.15 (t, 1H, *J* = 8.1 Hz, CH$_2$CHPh$_2$), 3.92 (d, 2H, *J* = 7.0, 5.9 Hz, CH$_2$CHPh$_2$), 3.25 (q, *J* = 6.7 Hz, 2H, CF$_2$CONHCH$_2$), 2.60 (br s, 2H, CH$_2$NH$_2$), 1.47 (m, 4H, CONHCH$_2$CH$_2$ + CH$_2$CH$_2$NH$_2$), 1.20 (m, 16H, alkyl chain); $^{13}$C NMR

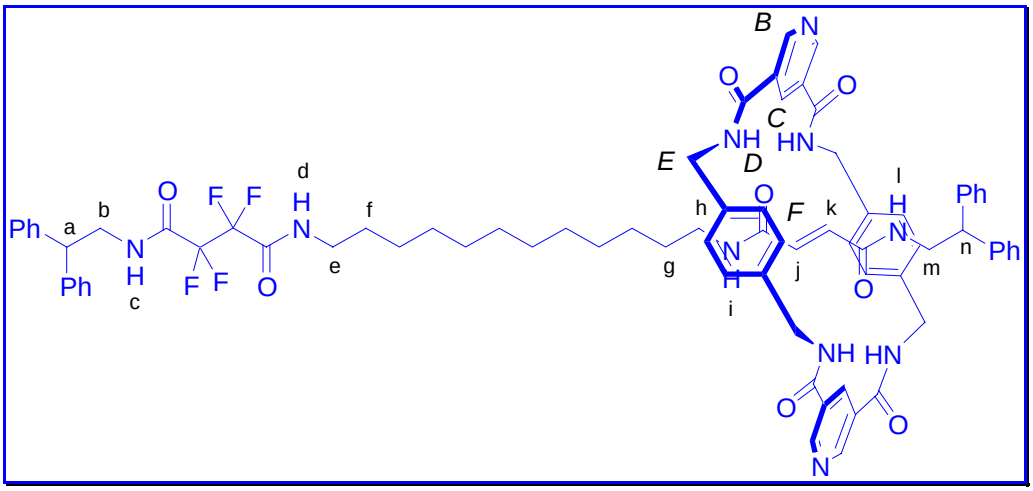
(100 MHz, $CDCl_3$): δ = 158.31, 157,73, 140.82, 128.83, 127.94, 127.12, 109.01, 104.73, 50.36, 44.19, 39.85, 29.61, 29.23, 29.01, 28.79, 28.92, 28.43, 25.32, 20.51; $^{19}F$ NMR (235 MHz, $CDCl_3$): δ = -120.65 (s, 2F, $CF_2$), -120.82 (s, 2F, $CF_2$); HRMS calcd. for $C_{30}H_{42}F_4N_3O_2$ [M+$H^+$] 552.66711 found (FAB, 3-NOBA matrix) 552.66352.

***(E)*-But-2-enedioic acid (2,2-diphenylethyl)-amide {12-[3-(2,2-diphenyl-ethylcarbamoyl)-2,2,3,3-tetrafluoropropionylamino]-dodecyl}-amide, *E*-2:**



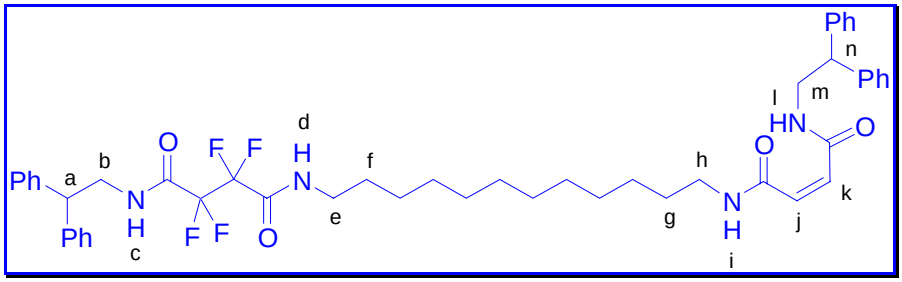

To a stirred solution of *N*-(12-aminododecyl)-*N'*-(2,2-diphenylethyl)-2,2,3,3-tetrafluorosuccinamide, **S3** (0.73 g, 1.33 mmol) in 15 mL of $CH_2Cl_2$ was added a suspension of (*E*)-3-(2,2-diphenylethylcarbamoyl)acrylic acid (0.39 g, 1.33 mmol) (prepared as described in A Altieri, G Bottari, F Dehez, D A Leigh, J K Y Wong and F Zerbetto, *Angew. Chem. Int. Ed.* 2003, **42**, 2296-2300) in 4 mL of THF. Triethylamine (0.5 mL) was then added until pH = 10 followed by BOP (0.88 g, 2.00 mmol). The resulting suspension was stirred at room temperature for 30 minutes, after which time a dark solution was obtained which was stirred for a further 3 h. Concentration under reduced pressure gave a viscous residue which was subjected to column chromatography (silica gel, 5:95 MeOH/$CHCl_3$) to yield the product as a colourless solid. 1.10 g (47%); m.p. 233-234 °C; $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.26 – 7.17 (m, 20H, Ph), 6.73 (d, 1H, *J* = 14.9 Hz, $H_j$), 6.62 (br s, 1H, $NH_c$), 6.60 (d, 1H, *J* = 14.9 Hz, $H_k$), 6.59 (br s, 1H, $NH_d$), 5.83 (br t, 1H, *J* = 5.1 Hz, $NH_i$), 5.71 (br t, 1H, *J* = 5.3 Hz, $NH_l$), 4.16 (t, 1H, *J* = 8.1 Hz, $H_a$), 4.14 (t, 1H, *J* = 8.4 Hz, $H_n$), 3.92 (m, 4H, $H_b$ + $H_m$), 3.24 (m, 4 H, $H_e$ + $H_h$), 1.51 (m, 4 H, $H_f$ + $H_g$), 1.28-1.16 (m, 16H, alkyl chain); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 165.06, 164.78, 159.83, 157.32, 141.74, 141.14, 132.89, 132.06, 128.64, 128.59, 127.88(x2), 126.89, 126.72, 117.95, 111.26, 50.20, 49.82, 44.30, 44.18, 39.88, 39.72, 32.03, 29.25 (x2), 29.20, 29.05, 28.96 (x2), 28.66, 26.75, 24.50; $^{19}F$ NMR (235 MHz, $CDCl_3$): δ = -120.08 (br s, 2F, $CF_2$), -120.35 (br s, 2F, $CF_2$); HRMS calcd. for $C_{48}H_{57}F_4N_4O_4$ [$(M+H)^+$] 829.43159) found (FAB, 3-NOBA matrix) 829.43199.

**Rotaxane *E*-1**



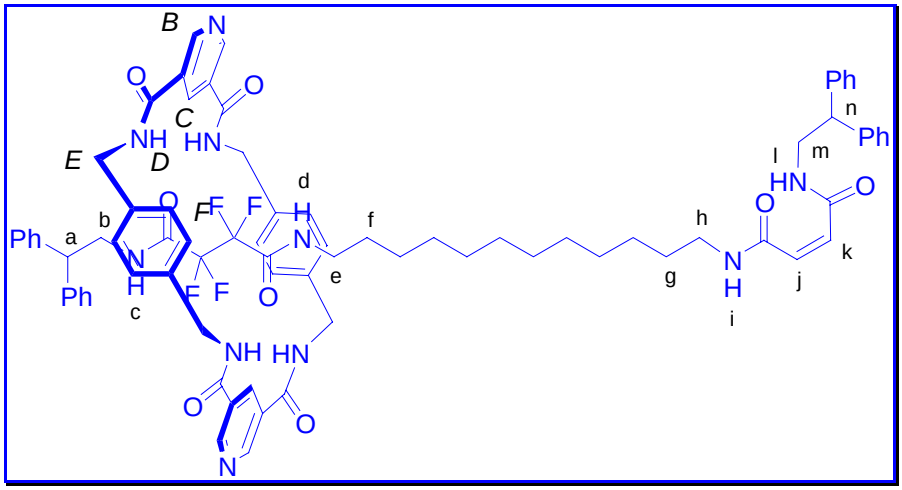
To a solution of *E*-**2** (0.24 g, 0.29 mmol) in 100 mL of $CHCl_3$:$CH_3CN$ (9:1) and $Et_3N$ (1.5 mL) were added simultaneously solutions of 3,5-pyrydinedicarbonyl dichloride (0.71 g, 3.5 mmol) in 20 mL of $CHCl_3$ and of *p*-xylylenediamine (0.47 g, 3.5 mmol) in 20 mL of $CHCl_3$ over a period of 3 hrs using motor-driven syringe pumps. After a further 3 h the resulting mixture was filtered and the filtrate concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel using a solvent gradient of $CHCl_3$ to $CHCl_3$/MeOH (94/6) to obtain the desired product as a colourless solid. 0.26 g (65%); m.p. 233-234 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ = 9.09 (s, 4H, $H_B$), 8.98 (br s, 1H, $NH_h$), 8.78 (s, 2H, $H_C$), 8.65 (br s, 1H, $NH_k$), 7.54 (br s, 4H, $NH_D$), 7.24 - 7.10 (m, 28H, $H_{Ar}$), 7.02 (br t, 1H, *J* = 5.4 Hz, $NH_c$), 5.71 (br t, 1H, *J* = 5.2 Hz, $NH_d$), 5.74 (d, 1H, *J* = 15.4 Hz, $H_j$), 5.69 (d, 1H, *J* = 15.6 Hz, $H_k$), 4.41 (br s, 8H, $H_E$), 4.16 (t, 1H, *J* = 8.0 Hz, $H_a$), 4.14 (t, 1H, *J* = 7.8 Hz, $H_n$), 3.90 (m, 2H, $H_b$), 3.86 (m, 2H, $H_m$), 3.21 (m, 2 H, $H_e$), 3.11 (m, 2 H, $H_h$), 1.44 (m, 2 H, $H_f$), 1.34 (m, 2 H, $H_g$), 1.28-1.10 (m, 16H, alkyl chain); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 165.86, 165.35, 163.85, 165.81, 157.70, 150.92, 141.40, 141.06, 136.63, 132.81, 130.04, 129.32, 128.87, 128.76, 128.74 (x2), 127.91, 127.72, 127.24, 127.01, 117.47, 111.92, 50.43, 49.91, 44.30, 44.14, 44.04, 39.93, 39.83, 29.29, 29.27, 29.20, 29.15, 29.10, 28.96, 28.87, 28.69, 26.93, 26.45; $^{19}$F NMR (235 MHz, $CDCl_3$): δ = -120.12 (d, 2F, *J* = 14.2 Hz, $CF_2$), -120.27 (d, 2F, *J* = 14.2 Hz, $CF_2$); HRMS calcd. for $C_{78}H_{82}F_4N_{10}O_8$ [M+$H^+$] 1362.62532 found (FAB, 3-NOBA matrix) 1362.62978.

**_(Z)_-But-2-enedioic acid (2,2-diphenylethyl)-amide {12-[3-(2,2-diphenyl-ethylcarbamoyl)-2,2,3,3-tetrafluoropropionylamino]-dodecyl}-amide, _Z_-2**




To a stirred solution of *N*-(12-aminododecyl)-*N'*-(2,2-diphenylethyl)-2,2,3,3-tetrafluorosuccinamide, **S3** (0.52 g, 0.94 mmol) in 30 mL of $CH_2Cl_2$ was added a suspension of (*Z*)-3-(2,2-diphenylethylcarbamoyl)acrylic acid (0.28 g, 0.94 mmol) (prepared as described in A Altieri, G Bottari, F Dehez, D A Leigh, J K Y Wong and F Zerbetto, *Angew. Chem. Int. Ed.* 2003, **42**, 2296-2300) in 3 mL of THF. Triethylamine (0.4 mL) was added until pH 10 followed by BOP (0.62 g, 1.41 mmol). The resulting mixture was stirred at room temperature for 3 h and concentrated under reduced pressure to give a viscous residue which was subjected to column chromatography (silica gel, 4:96 MeOH/$CHCl_3$) to afford the product as a colourless solid. 0.78 g (65%); m.p. 165-167 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.30 (br t, 1H, *J* = 5.6 Hz, $NH_i$), 7.56 (br t, 1H, *J* = 5.3 Hz, $NH_l$), 7.27 - 7.13 (m, 20H, Ph), 6.52 (br s, 2H, $H_c$ + $H_d$), 5.94 (d, 1H, *J* =13.4 Hz, $H_j$), 5.84 (d, 1H, *J* =13.4 Hz, $H_k$), 4.18 (t, 1H, *J* = 8.1 Hz, $CH_a$), 4.15 (t, 1H, *J* = 7.8 Hz, $CH_n$), 3.93 (dd, 2H, *J* = 7.8, 6.1 Hz, $CH_b$), 3.87 (dd, 2H, *J* = 7.8, 5.6 Hz, $CH_m$), 3.23 (td, 2H, *J* = 7.1, 6.6 Hz, $CH_e$), 3.18 (td, 2H, *J* = 7.1, 6.6 Hz, $CH_h$), 1.47 (m, 4 H, $H_f$ + $H_g$), 1.27-1.14 (m, 16H, alkyl chain); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 164.72 (x2), 159.10, 158.92, 141.65, 140.84, 133.71, 131.05, 128.83, 128.69, 127.99, 127.90, 127.12, 126.84, 116.11, 110.15, 50.24, 50.00, 44.08, 43.94, 39.98, 39.79, 29.35, 29.32, 29.28,29.12,29.00, 28.84, 26.87, 26.53, 25.57, 24.91; $^{19}$F NMR (235 MHz, $CDCl_3$): δ = -120.09 (d, 2F, *J* = 2.5 Hz, $CF_2$), -120.27 (d, 2F, *J* = 3.2 Hz, $CF_2$); HRMS calcd. for $C_{48}H_{57}F_4N_4O_4$ [M+$H^+$] 829.43159 found (FAB, 3-NOBA matrix) 829.43215.

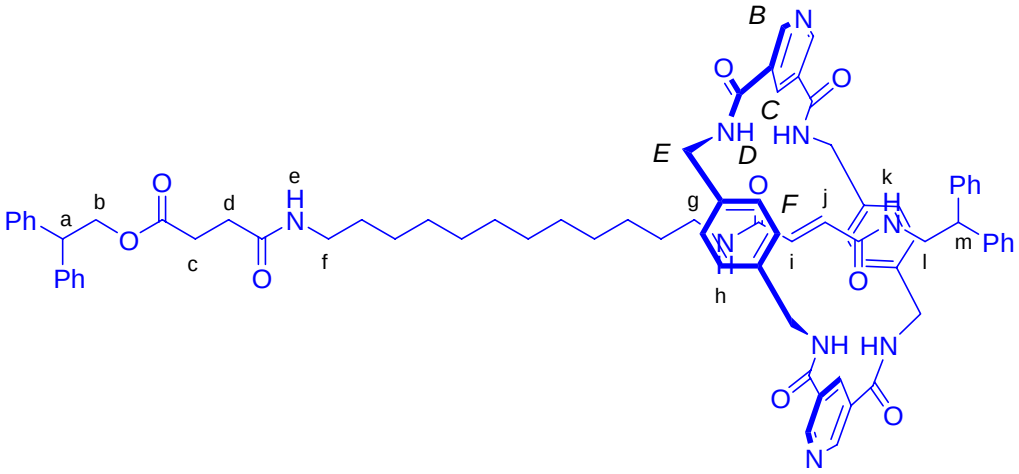
**Rotaxane *Z*-1**



Rotaxane *E*-**1** (10 mg, 0.005 mmol) was dissolved in $CH_2Cl_2$ (20 mL) and the solution placed in a quartz vessel, 5 equivalents of trifluoroacetic acid were added and the solution was degassed by bubbling $N_2$ for 10 minutes. The solution was directly irradiated at 254 nm using a multilamp photo-reactor (Model MLU18, Model 3022 lamps, Photochemical Reactors Ltd., Reading, UK.) for 5 minutes. The progress of the photoisomerization was monitored by TLC ($CHCl_3$/MeOH 94:6) or $^1$H NMR ($CDCl_3$). After the photostationary state (50:50 by $^1$H NMR) was reached the reaction mixture was concentrated under reduced pressure, then redissolved in $CH_2Cl_2$ (5 mL) and washed with sat. $Na_2CO_3$ (1 x 5 mL) and brine (1 x 5 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and the filtrate concentrated. The resulting solid was subjected to column chromatography on silica gel using a solvent gradient of $CHCl_3$ to $CHCl_3$/MeOH (90/10) to obtain the desired product as a colourless solid. yield = 48%. Alternatively, to a solution of *Z*-**1** (0.22 g, 0.27 mmol) in 100 mL of $CHCl_3$ and $Et_3N$ (1.4 mL, 9.75 mmol) were added simultaneously solutions of 3,5-pyrydinedicarbonyl dichloride (0.66 g, 3.25 mmol) in 20 mL of $CHCl_3$ and of *p*-xylylenediamine (0.44 g, 3.25 mmol) in 20 mL of $CHCl_3$ over a period of 3 hrs using motor-driven syringe pumps. After a further 3 h the resulting suspension was filtered and the filtrate concentrated under reduced pressure to afford the crude product which was purified as described above. m.p. 193-195 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 9.27 (s, 4H, $H_B$), 8.88 (s, 2H, $H_C$), 8.68 (br t, 1H, $J$ = 4.8 Hz, $NH_i$), 8.57 (br t, 1H, $J$ = 5.3 Hz, $NH_l$), 7.81

(br s, 4H, $NH_D$), 7.31 (br t, 1H, $J$ = 5.6 Hz, $NH_c$), 7.27 - 7.08 (m, 16H, $H_{Ar}$), 7.00 (s, 8H, $H_F$), 6.92 (d, 4H, $J$ = 7.1 Hz, $H_{Ar}$), 6.80 (br t, 1H, $J$ = 5.8 Hz, $NH_d$), 5.75 (d, 1H, $J$ = 13.4 Hz, $H_j$), 5.62 (d, 1H, $J$ = 13.4 Hz, $H_k$), 4.61 (dd, 4H, $J$ = 14.0, 6.2 Hz, $H_E$), 4.26 (dd, 4H, $J$ = 14.0, 4.0 Hz, $H_{E'}$), 4.17 (t, 1H, $J$ = 7.8 Hz, $H_a$), 3.96 (t, 1H, $J$ = 7.8 Hz, $H_n$), 3.91 (dd, 4H, $J$ = 7.1, 6.1 Hz, $H_b$), 3.57 (m, 2H, $H_m$), 3.16 (m, 2 H, $H_e$), 3.04 (m, 2 H, $H_h$), 1.56 (m, 2 H, $H_f$+$H_g$), 1.28-1.10 (m, 16H, alkyl chain); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 164.44, 164.18, 160.24, 157.85 (x2), 152.54, 140.97, 140.06, 136.97,134.51, 133.04, 131.52, 129.38, 128.81, 128.27, 127.90, 127.56, 127.10, 112.70, 107.46, 44.20, 44.01, 43.96, 39.96, 39.62, 30.52, 29.74, 29.00, 28.94 (x2), 28.92, 28.70, 28.67, 28.52, 27.39, 26.03, 25.22; $^{19}$F NMR (235 MHz, $CDCl_3$): δ -120.75 (s, 2F, $CF_2$), -121.11 (s, 2F, $CF_2$); HRMS calcd. for $C_{78}H_{82}F_4N_{10}O_8$ [M+$H^+$] 1362.62532 found (FAB, 3-NOBA matrix) 1362.62332.

**Non-Fluorinated rotaxane control, *E*-S4**




Rotaxane *E*-**S4** was synthesized from thread *E*-**S5**[A. Altieri, G. Bottari, F. Dehez, D. A. Leigh, J. K. Y. Wong, F. Zerbetto, *Angew. Chem.* **2003**, *115*, 2398-2402; *Angew. Chem., Int. Ed.* **2003**, *42*, 2296-2300] using analogous methods to those described above for *E*-**1** in 59 % yield. m.p. > 300°C; $^1$H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.43 (brt, 1H, $H_h$), 9.16 (s, 4H, $H_B$), 8.85 (s, 2H, $H_C$), 7.62 (brs, 4H, $H_D$), 7.30-7.19 (m, 21H, $H_{Ph}$ + $H_k$), 5.86 (brs, 2H, $H_i$ + $H_j$), 5.74 (brt, 1H, $H_e$), 4.61 (d, 2H, $J$ = 7.3 Hz, $H_b$), 4.52 (brs, 8H, $H_E$), 4.33 (t, 1H, $J$ = 7.3 Hz, $H_a$), 4.25 (t, 1H, $J$ = 7.6 Hz, $H_m$), 3.95 (brs, 2H, $H_l$), 3.15 (m, 2H, $H_f$), 3.04 (2H, $H_g$), 2.54 (t, 2H, $J$ = 6.6 Hz, $H_c$), 2.32 (t, 2H, $J$ = 6.6 Hz, $H_d$), 1.51-1.36 (m, 4H, $C\underline{H}_2$-$CH_f$ + $C\underline{H}_2$-$CH_g$), 1.21 (brs, 16H, $H_{alkyl}$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 172.89, 171.25, 166.14, 165.60, 163.31, 157.72, 150.91,

141.42, 141.02, 136.76, 129.73, 128.95, 128.65, 128.58, 128.18, 127.78, 127.32, 126.82, 66.89, 50.52, 49.74, 45.85, 39.63, 30.97, 29.65, 29.54, 29.50, 29.22, 29.12, 27.12, 26.86. HRMS calcd. for $C_{78}H_{86}N_9O_9$ [M + $H^+$] 1292.65485 found (FAB, 3-NOBA matrix) 1292.63261.

## II. Surface preparation and contact angle and transport experiments

### Materials.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecanethiol was synthesized according to a procedure of Naud et al.[*J. Fluor. Chem*. **104**, 173 (2000)] by Bert de Boer, Materials Science Centre, University of Groningen. 10-Carboxy-1-decanethiol (11-MUA) [CAS 71310-21-9] of HPLC purity better than 97% was purchased from Dijondo, Japain, chloroform [CAS 67-66-3] of HPLC purity better than 99.9% was purchased from Aldrich, diiodomethane [CAS 75-11-6] of purity better than 99%, and dichloromethane [CAS 75-09-2] of purity better than 99.8% were purchased from Acros Organics, Belgium, formamide [CAS 75-12-7] and ethanol [CAS 64-17-5] of purity better than 99% were purchased from Merck, Germany. All chemicals were used without further purification. The gold on glass substrates were 250 nm thickness Au deposited on chromium layers of 2.5 nm thickness on glass plates and were obtained from Arrandee, Germany. The gold on mica substrates were prepared by evaporation of 99.99% gold, Umicore Materials AG, on freshly cleaved mica sheets, Ted Paella, Inc., at $10^{-7}$ mbar in a custom-built evaporator in the Materials Science Centre, University of Groningen.

### Preparation of Self-Assembled Monolayers (SAM's)

The gold on glass substrates were flame annealed, cleaned in an ozone discharge for 15 minutes, and sonicated in ethanol for 20 minutes immediately before use. The

mica on gold substrates were flame annealed immediately before use. Carboxylic acid-terminated SAMs were prepared by immersing the gold substrates in 1 mM chloroform solution of 11-MUA and kept in a dark place at room temperature for 21 h. The F-terminated SAMs were prepared by immersing the gold substrates in a 1 mM ethanol solution of heptadecafluorodecanethiol and kept in a dark place at room temperature for 21 h. The samples were rinsed three times with the solvent and dried under argon before contact angle measurements.

The properties of the 11-MUA SAMs on Au(111) have been described elsewhere[2,3]. Briefly, the 11-MUA forms well ordered carboxylic acid-terminated monolayers on gold substrates. The water used in the droplet experiments was doubly distilled and demineralized (Milli-Q, 18.0 MΩ). The contact angle of the water drop obtained for the 11-MUA SAM without a physisorbed rotaxane, 30s after drop deposition was 5 ± 2°, and during the following minute the drop wetted the surface completely, as expected for a hydrophilic surface[3,4].

The procedures of grafting rotaxanes containing a pyridine function in the macrocyclic component on carboxylic-terminated SAMs have been described in earlier papers[3,5,6]. Briefly, the rotaxanes *E*-**1** and *E*-**S4** are physisorbed on the acid-terminated surface by hydrogen bonding between the pyridine group of the macrocycle and the carboxylic acid of the 11-MUA SAM.

The contact angle of the water drop on *E*-**1** and *E*-**S4** grafted on 11-MUA measured 30 seconds after deposition were 55 ± 2° and 45 ± 2° for *E*-**1** and *E*-**S4**, respectively. The contact angle of water drop deposited on the heptadecafluorodecanethiol SAM was 98 ± 2°, as expected for a highly hydrophobic surfaces[1,7].

The hysteresis ($\cos \theta_a - \cos \theta_r$) of diiodomethane (viscosity $\eta = 2.76$ mPa) obtained from dynamically advancing and receding contact lines on the gradient surface of these experiments is smaller (0.004) than the theoretical value (0.22) calculated using the equation proposed by Daniel et al. (Daniel, S. & Chaudhury, M. K., Rectified Motion of Liquid Drops on Gradient Surfaces Induced by Vibration. *Langmuir* **18**, 3404-3407 (2002); Daniel, S., Sircar, S., Gliem, J. & Chaudhury, M. K., Ratcheting Motion of Liquid Drops on Gradient Surfaces, *Langmuir* **20**, 4085-4092 (2004)) Similar discrepancies have previously been observed for viscous liquids such as ethylene glycol ($\eta = 2.65$ mPa), where the viscous bending of the drop near the contact lines is sufficient to interfere with the measurement of true hysteresis.

## III. XPS Measurements

The XPS measurements were performed using an X-PROBE Surface Science Laboratories photoelectron spectrometer with a monochromatic Al $K_\alpha$ X-ray source ($h\nu$=1486.6 eV). The energy resolution was set to 1.5 eV to minimize data acquisition time and the photoelectron take off angle was 37°. The binding energies were referenced to the Au $4f_{7/2}$ core level[8]. The base pressure in the spectrometer was $1x10^{-10}$ Torr. A minimum number of scans were accumulated to minimize any possible X-ray induced damage[9-12].

Spectral analysis included a background subtraction and peak separation using mixed Gaussian-Lorentzian functions in a least squares curve-fitting program (Winspec) developed in the LISE laboratory of the Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium. The procedure consisted in fitting a minimum number of peaks that can reproduce the spectral raw data and are consistent with the molecular structure of the film, with the simplification of assuming equivalent atoms for chemical

environments of the same element that give very similar values of the binding energy. The photoemission peak areas of each element were normalized by the sensitivity factors of each element tabulated for the spectrometer used in these measurements[8].

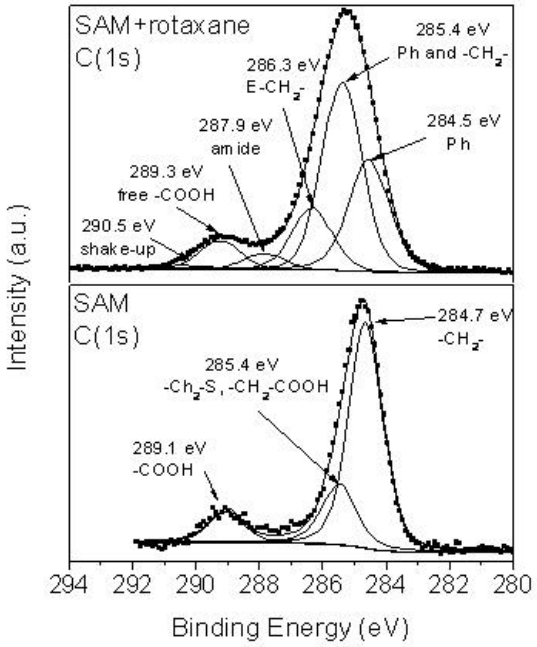



Figure S1.

Figure S1 shows the carbon 1s core level photoemission spectra for 11-MUA self-assembled monolayer on Au substrate (bottom panel) and for the same monolayer functionalized with *E*-**1** (top panel). No chlorine was detected in the photoemission spectra (not shown), hence we can exclude incorporation of solvent molecules ($CH_2Cl_2$ or $CHCl_3$) into these films and assume that the C signals are due solely to the *E*-**1** and SAM molecules. In the case of the 11-MUA SAM (bottom panel) we need a minimum of three components to reproduce the experimental lineshape: one at 284.6 eV, corresponding to aliphatic carbon, a second one at 285.4 eV originating from thiol carbon and β-carbon of the carboxylic group, and a third one at 289.0 eV, deriving from carboxylic carbon. These results are in good agreement with previous reports[13,14]. From

the spectral analysis of *E*-**1** grafted on the 11-MUA SAM (top panel), six main components can be distinguished. Although there are more than six distinct carbon environments in this film, in practice XPS can not distinguish between all the different phenyl-ring and aliphatic carbons. It is immediately apparent that there are several differences between this spectrum and the one of 11-MUA SAM alone. The first peak at 284.5 eV, accompanied by the shake-up feature due to $\pi$-$\pi^*$ transitions (290.5 eV), is unambiguously assigned to aromatic carbon, and confirms the presence of *E*-**1**. The peak at 285.4 eV originates from different contributions, namely, from carbon atoms of the aliphatic chains both on *E*-**1** and on 11-MUA SAM, and from aromatic carbon atoms bound to electronegative groups. This explains why its intensity is important also after functionalization by rotaxanes. The component at 286.3 eV is due to aliphatic carbon atoms bound to electronegative carboxylic and amide groups. Peaks characteristic of amide and carboxylic carbons are observed at 287.9 eV and 289.3 eV[15-17]. The signal of carbons bond to fluorine is too weak to be seen in the photoemission line.

The clearest evidence that *E*-**1** is successfully grafted on the surface comes from the nitrogen 1s and fluorine 1s core levels. Figure S2 shows the nitrogen 1s photoemission spectrum, where the single peak at 400.4 eV corresponds to amide nitrogen[13-15]. Figure 3 presents the F 1s photoemission line, with a maximum at 688.6 eV[8].

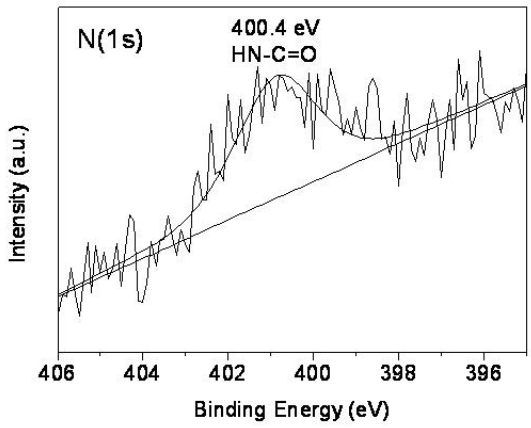



Figure S2

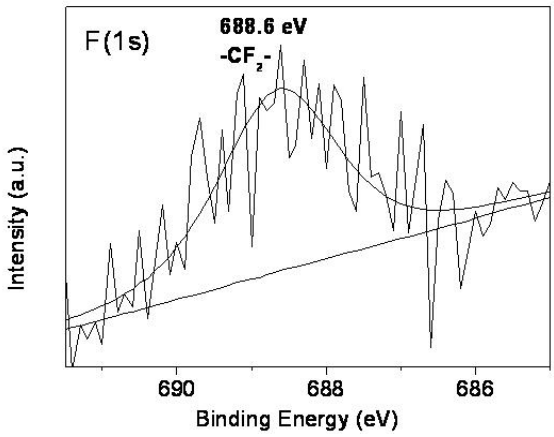



Figure S3

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