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Supporting Information

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Muscle-like Supramolecular Polymers: Integrated Motion from Thousands of Molecular Machines**

Guangyan Du, Emilie Moulin, Nicolas Jouault, Eric Buhler, and Nicolas Giuseppone**

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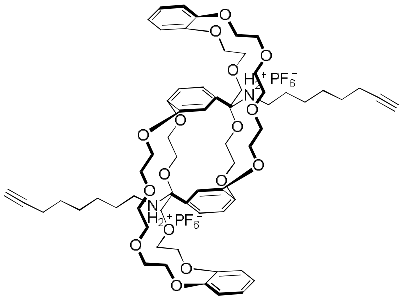
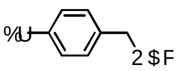
Synthetic procedures and products characterizations

All *reagents and solvents* were purchased at the highest commercial quality and used without further purification unless otherwise noted. All reactions were carried out under an atmosphere of argon unless otherwise stated. Dry solvents were obtained using a double column SolvTech purification system. Microwave reactions were carried out with a single mode cavity Discover Microwave Synthesizer (CEM Corporation, NC, USA), producing continuous irradiation at 2455 MHz and equipped with simultaneous external air-cooling system. Yields refer to spectroscopically purified homogeneous materials (*^{1}H NMR*). *Thin Layer Chromatographies* were performed with TLC silica plastic sheets (Polygram SIL G/UV$_{254}$, Macherey-Nagel) or TLC alox plastic sheets (Polygram Alox N/UV$_{254}$, Macherey-Nagel). In most cases, irradiation using a *Bioblock VL-4C* UV-Lamp (6 W, 254 nm and/or 365 nm) as well as 10% ethanolic phosphomolybdic acid and Ce-molybdate stainings were used for visualization. *Preparative Adsorption Flash Column Chromatographies* were performed using silica gel (Geduran, silica gel 60 (230 –400 mesh, 40 – 63 µm, Merck)) and aluminium oxide 90 (Merck; 70 - 230 mesh, standardized activity II). *ESI-MS spectra* were performed on a Waters SQD mass spectrometer (sample solutions were introduced into the mass spectrometer source with a syringe pump with a flow rate of 20 µL.min^{-1}). *MALDI spectra* were recorded on a Bruker Daltonics AutoflexII TOF spectrometer. *^{1}H NMR spectra* were recorded either on a *Bruker Avance 400* spectrometer at 400 MHz or on a *Bruker Avance 400* spectrometer at 500 MHz and ^{13}C *NMR* spectra either at 100 MHz or 125 MHz. The spectra were internally referenced to the residual proton solvent signal. Residual solvent peaks were taken as reference ($CDCl_3$: 7.26 ppm, CD_3OD: 3.31 ppm, CD_3CN: 1.94 ppm). For *^{1}H NMR* assignments, the chemical shifts are given in ppm. The following notation is used for the *^{1}H NMR* spectral splitting patterns: singlet (s), doublet (d), triplet (t), quadruplet (q), multiplet (m), broad (br).

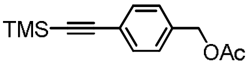


Pseudorotaxane (8). This compound was synthesized according to the procedure described by F. Coutrot *et al.* *(1)*

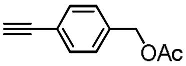
^{1}H NMR (CDCl$_3$, 400 MHz, 25°C): d = 6.91 (d, *J* = 8.3Hz, 2H), 6.84-6.71 (m, 10H), 6.57 (s, 2H), 4.44-4.38 (m, 2H), 4.35-4.29 (m, 2H), 4.23-3.63 (m, 48H), 3.56-3.36 (m, 4H), 2.09 (td, *J* = 6.9, 1.8Hz, 4H), 1.92 (brs, 2H), 1.48-1.14 (m, 16H); ^{13}C NMR (CDCl$_3$, 100 MHz, 25°C): d = 147.9, 147.8, 147.8, 147.0, 146.5, 146.3, 124.8, 123.2, 121.4, 121.2, 113.4, 112.7, 112.1, 112.0, 84.4, 72.6, 72.0, 71.3, 71.0 (x3), 70.6, 70.5, 68.8, 68.7, 67.8, 67.2, 67.1 (x2), 66.9, 52.4, 49.0, 28.2, 26.8, 26.4, 18.4; ESI-MS: calcd. for $C_{66}H_{96}N_2O_{16}P_2F_{12}$: 586.84 [M-2PF$_6$]$^{2+}$, found: 586.45.



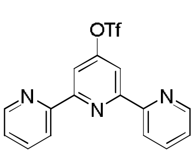
4-Bromobenzyl acetate (2). *(2)* A solution of 4-bromobenzyl alcohol (4.00 g, 21.4 mmol) and DMAP (268 mg, 2.14 mmol) in a 1:1 mixture of acetic anhydride/pyridine (40 mL) was stirred at room temperature for 22 h until the starting material had been consumed as determined by TLC analysis. Water (10 mL) and ethyl acetate (10 mL) were then added, and the layers were separated. The organic layer was washed with HCl$_{aq}$. (10 mL, 1 M) and brine (10 mL). The organic layer was then dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. Further purification by flash chromatography (SiO$_2$, *n*-hexane/EtOAc: 95/5) afforded compound **1** (4.45 g, 91%) as a pale yellow solid. R$_f$ = 0.45 (*n*-hexane / EtOAc : 20/1); ^{1}H NMR (CDCl$_3$, 400 MHz, 25°C): d = 7.48 (d, *J* = 8.4Hz, 2H), 7.23 (d, *J* = 8.3Hz, 2H), 5.05 (s, 2H), 2.10 (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz, 25°C): d = 170.9, 135.1, 131.8, 130.1, 122.4, 65.6, 21.1; ESI-MS: calcd for $C_9H_9BrO_2$: 228.99 [M+H]$^+$, found 229.13.



4-Trimethylsilylbenzyl acetate (3). *(3)* Trimethylsilyl acetylene (3.34 ml, 24 mmol) was added to a solution of CuI (767 mg, 4 mmol), $PdCl_2(PPh_3)_2$ (1.41 g, 2 mmol), PPh_3 (1.06 g, 4 mmol) and 4-bromobenzylacetate (4.61 g, 20 mmol) in triethylamine (30 mL). The mixture was degassed by using freeze-thaw cycles and heated up to 70 °C for 36 h under a nitrogen atmosphere. The resulting dark brown mixture was then filtered and the solvent was removed in vacuo. Further purification by column chromatography (SiO_2, *n*-hexane/EtOAc: 20/1) provided compound **3** (4.56 g, 89%) as a pale yellow solid. $R_f = 0.2$ (*n*-hexane/EtOAc: 20/1); ^1H NMR ($CDCl_3$, 400 MHz, 25°C): d = 7.44 (d, *J* = 8.4Hz, 2H), 7.30 (d, *J* = 8.4Hz, 2H), 5.07 (s, 2H), 2.08 (s, 3H), 0.25 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz, 25°C): d = 170.9, 136.4, 132.3, 128.0, 123.2, 104.8, 94.8, 65.9, 21.1, 0.1; ESI-MS: calcd for $C_{14}H_{18}O_2Si$: 247.12 $[M+H]^+$, found 247.15.

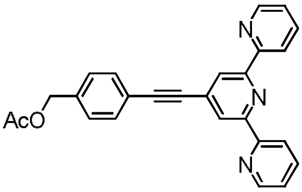


4-ethynylbenzyl acetate (4). A solution of 4-trimethylsilylbenzyl acetate (1.82 g, 8.9 mmol) in THF (10 mL) was treated with TBAF (1M solution in THF, 0.8 mL, 0.8 mmol). The mixture was stirred at room temperature for 30 min and the solvent was removed under reduced pressure. Further purification by column chromatography (SiO_2, *n*-hexane/EtOAc: 20/1) provided compound **3** (1.10 g, 85%) as a pale yellow solid. $R_f = 0.2$ (*n*-hexane/EtOAc: 20/1); ^1H NMR ($CDCl_3$, 400 MHz, 25°C): d = 7.48 (d, *J* = 8.2Hz, 2H), 7.31 (d, *J* = 8.4Hz, 2H), 5.09 (s, 2H), 3.09 (s, 1H), 2.11 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 25°C): d = 170.9, 136.8, 132.5, 128.2, 122.2, 83.4, 77.7, 65.9, 21.1; Anal. calcd. for $C_{11}H_{10}O_2$: C 75.84, H 5.79; found C 75.17, H 5.86.

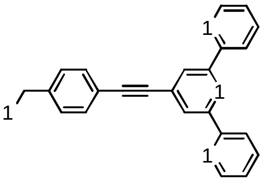


4'-[(Trifluoromethyl)sulfonyl]oxy]-2,2':6',2"-terpyridine (5). Terpyridone (6.68 g, 27.0 mmol) was dissolved in pyridine (70 mL) and the reaction mixture was cooled down to 0°C. Trifluoromethanesulfonic anhydride (4.5 mL, 27.0 mmol) was added and the mixture was stirred overnight at room temperature. Ice (45.0 g) was then added to the reaction mixture. The white precipitate that formed was filtered, washed with cold water to give compound **5** (10.3 g, 100%) as a white solid. ^1H NMR ($CDCl_3$, 400 MHz, 25°C): d = 8.72 (d, *J* = 4.8Hz, 2H), 8.62 (d, *J* =

7.8Hz, 2H), 8.42 (s, 2H), 7.89 (ddd, *J* = 7.7, 7.7, 1.7Hz, 2H), 7.39 (ddd, *J* = 7.4, 4.8, 1.0Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, 25°C): d = 159.0, 158.7, 154.5, 149.6, 137.2, 124.9, 121.6, 118.7 (q, J_{CF} = 320Hz), 113.3; ESI-MS: calcd for $C_{16}H_{10}N_3O_3F_3S$: 382.05 $[M+H]^+$, found 382.08; Anal. calcd for $C_{16}H_{10}N_3O_3F_3S$: C 50.40, H 2.64, N 11.02, found: C 50.05, H 2.81, N 10.91.



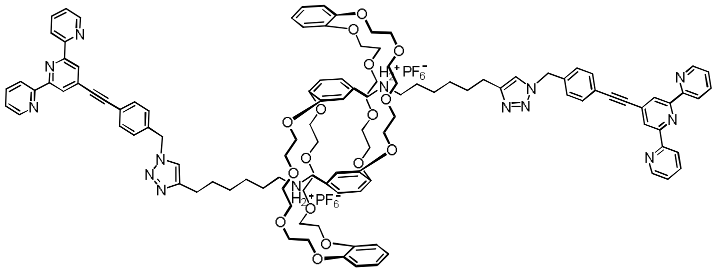
2,2':6,2?-terpyridinethynylbenzyl acetate (6). 2,2':6,2?-terpyridine triflate (2.12 g, 5.56 mmol) was added to a solution of compound **4** (1.26 g, 7.23 mmol) in a mixture of triethylamine (40 mL) and tetrahydrofuran (10 mL). The mixture was degassed by using freeze-thaw cycles and $Pd(Ph_3)_4$ (642 mg, 0.56 mmol) was added. The mixture was degassed once more by using freeze-thaw cycles and then heated up to 65°C overnight under a nitrogen atmosphere. The resulting dark brown mixture was filtered and the solvent was removed in vacuo. Further purification by column chromatography (Al_2O_3, *n*-hexane/CH_2Cl_2: 10/1) yielded compound **4** (1.60 g, 71%) as a white solid. R_f = 0.6 (Al_2O_3, *n*-hexane/CH_2Cl_2: 10/1); ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): d = 8.72 (ddd, *J* = 4.8, 1.7, 0.9Hz, 2H), 8.62 (ddd, *J* = 8.0, 1.0, 1.0Hz, 2H), 8.58 (s, 2H), 7.87 (ddd, *J* = 7.8, 7.7, 1.8Hz, 2H), 7.57 (d, ^3J = 8.2Hz, 2H), 7.39-7.34 (m, 4H), 5.13 (s, 2H), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 25°C): d = 170.9, 155.8, 155.7, 149.3, 137.1, 137.0, 133.4, 132.3, 128.3, 124.2, 123.0, 122.5, 121.4, 93.4, 88.0, 65.9, 21.1; ESI-MS: calcd for $C_{26}H_{19}N_3O_2$: 406.16 $[M+H]^+$, found 406.22.



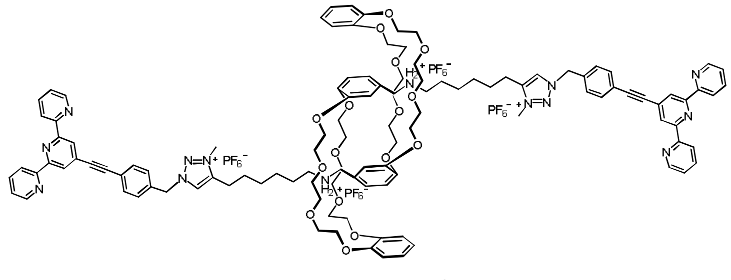
2,2':6,2?-terpyridineethynylbenzyl azide (7). A solution of compound **6** (1.6 g, 3.9 mmol) in a mixture of dichloromethane/methanol (9:1, 60 mL) was treated with sodium hydroxide (320 mg, 12 mmol) and the solution was stirred at room temperature for 1h. The solvent was then removed in vacuo, and the resulting mixture was dissolved with a mixture of CH_2Cl_2 (50 mL) and water (50 mL). The pH was then ajusted to 5~6 using dilute HCl (2M), and the aqueous phase was extracted with CH_2Cl_2 (50 mL) and EtOAc (3*50 mL). The organic phases were combined, dried over Na_2SO_4, and evaporated in vacuo to give 2,2':6,2?-terpyridineethynylbenzyl alcohol, which was pure enough to be used as such in the next step. ^1H NMR ($CDCl_3$, 400 MHz, 25°C): d = 8.74 (d, *J* = 4.2Hz, 2H), 8.65 (d, *J* = 7.9Hz, 2H), 8.59 (s, 2H), 7.90 (ddd, *J* = 7.8, 7.8, 1.5Hz, 2H), 7.58 (d, *J* = 8.2Hz, 2H), 7.41-7.36 (m, 4H), 4.75 (s, 2H).

A solution of crude 2,2':6,2?-terpyridineethynylbenzyl alcohol in CH_2Cl_2 (10 mL) was cooled down to 0°C and triethylamine (1.5mL, 10.8 mmol) and methanesulfonyl chloride (1.0mL, 12.9 mmol) were added. The reaction mixture was then stirred overnight at room temperature and further dissolved with CH_2Cl_2 (70 mL). The organic phase was then extracted with water (50 mL) and $NH_4Cl_{sat.}$ (20 mL), dried over Na_2SO_4 and concentrated in vacuo to provide the mesylated derivative, which was pure enough to be used as such in the next step.

A solution of crude 2,2':6,2?-terpyridineethynylbenzylmesylate in a 1:1 mixture of DMF and THF (10 mL) was treated with sodium azide (1.5 g, 23 mmol) and heated up overnight to 50°C. After cooling down to room temperature, the reaction mixture was diluted with CH_2Cl_2 (70 mL). The organic phase was then extracted with water (50 mL) and $NH_4Cl_{sat.}$ (20 mL), dried over Na_2SO_4 and concentrated in vacuo. Further purification by column chromatography (Al_2O_3, *n*-hexane/CH_2Cl_2: 10/1) provided compound **7** (900 mg, 66% over 3 steps) as a white solid. R_f = 0.7 (*n*-hexane/CH_2Cl_2: 10/1? CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz, 25°C): d = 8.71 (d, *J* = 4.7Hz, 2H), 8.60 (d, *J* = 8.0Hz, 2H), 8.57 (s, 2H), 7.85 (ddd, *J* = 7.8, 7.8, 1.8Hz, 2H), 7.58 (d, *J* = 8.2Hz, 2H), 7.35-7.32 (m, 4H), 4.37 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, 25°C): d = 155.7, 155.7, 149.3, 137.0, 136.5, 133.3, 132.5, 128.3, 124.1, 122.9, 122.6, 121.3, 93.3, 88.2, 54.4; ESI-MS: calcd for $C_{24}H_{16}N_6$: 389.15 $[M+H]^+$, found: 389.21.

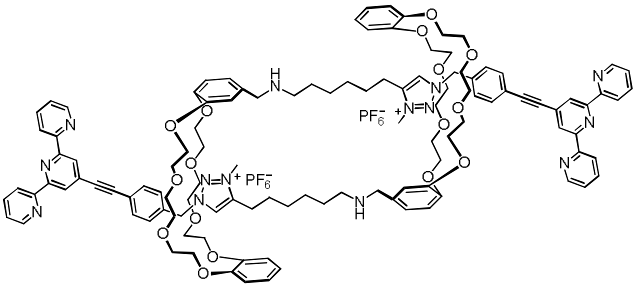


bis-2,2':6,2?-terpyridine rotaxane (9). To a solution of terpyridine azide **7** (106 mg, 0.27 mmol) and pseudo-rotaxane **8** (200 mg, 0.13 mmol) in a mixture of dry CH_2Cl_2 (10 mL) and dry CH_3CN (4 mL) were added successively $Cu(CH_3CN)_4PF_6$ (408 mg, 1.08 mmol) and 2,6-lutidine (128 µL, 1.08 mmol). The reaction mixture was stirred for 5 min, then heated by microwave irradiation (50 W) for 1h at 30°C and finally, stirred with an aqueous EDTA-disodium salt solution adjusted to a pH˜ 8-9 (20 mL). The mixture was then extracted with a 3:1 mixture of CH_2Cl_2/CH_3CN (3*20 mL). The organic phases were combined, dried over Na_2SO_4 and finally evaporated in vacuo. Further purification by column chromatography (Al_2O_3, CH_2Cl_2 ? CH_2Cl_2/CH_3OH: 100/1) yielded compound **9** (220 mg, 72%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): d = 8.71 (d, *J* = 4.1Hz, 4H), 8.62 (d, *J* = 7.9Hz, 4H), 8.56 (s, 4H), 7.87 (dd, *J* = 7.9, 7.2Hz, 4H), 7.57 (d, *J* = 8.1Hz, 4H), 7.36 (brdd, *J* = 6.1, 5.9Hz, 4H), 7.29 (d, *J* = 7.8Hz, 4H), 7.23 (s, 2H), 6.94-6.59 (m, 14H), 5.53 (s, 4H), 4.49-4.25 (m, 4H), 4.24-3.62 (m, 48H), 3.54-3.28 (m, 4H), 2.62 (t, *J* = 8.1Hz, 4H), 1.75-1.54 (m, 8H), 1.39-1.27 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz, 25°C): d = 155.8, 155.7, 149.4, 148.6, 147.8, 147.7, 146.5, 146.2, 137.1, 136.1, 133.2, 132.7, 128.3, 124.8, 124.3, 123.1, 123.0, 122.9, 121.4, 121.3, 121.2, 120.8, 113.2, 112.8, 112.0(x2), 92.9, 88.5, 72.4, 72.0, 71.4, 71.0, 70.9, 70.5, 70.1, 69.6, 67.7, 67.2, 67.1, 66.9, 53.8, 52.3, 48.9, 29.2, 28.7, 26.8, 26.7, 26.6, 25.6; MALDI-TOF: m/z calcd for $C_{114}H_{128}N_{14}O_{16}P_2F_{12}$: 974.48 $[M-2PF_6]^{2+}$, found: 974.64.



bis-2,2':6,2?-terpyridine methylated rotaxane (1^{ext}). Rotaxane **9** (45 mg, 0.02 mmol) and $Cu(OTf)_2$ (21.8 mg, 0.06 mmol) were dissolved in a 1:1 mixture of chloroform and acetonitrile

(6 mL). After stirring for 1h at room temperature, the solvents were evaporated in vacuo and a 1:1 mixture of iodomethane and acetonitrile (4 mL) was added. The mixture was stirred for 5 days at room temperature and, then solvents were evaporated in vacuo and the resulting solid was washed with Et_2O (10 mL) to give brown solid. This crude solid was dissolved in CH_2Cl_2 (20 mL) and the solution was stirred with an aqueous EDTA-disodium salt solution adjusted to a pH˜ 8-9 (20 mL). The mixture was then extracted with a 3:1 mixture of CH_2Cl_2/CH_3CN (3*20 mL). The organic phases were combined, dried over Na_2SO_4 and finally evaporated in vacuo. To a solution of this crude residue in water (4 mL) was added NH_4PF_6 (30 mg, 0.18 mmol) and a 3:1 mixture of CH_2Cl_2/CH_3CN (4 mL). The biphasic solution was stirred vigorously for 1h. The aqueous layer was extracted with $CHCl_3$ (3*20 mL). The organic layers were combined, dried over Na_2SO_4 and concentrated in vacuo to give product $\mathbf{1}^{\mathit{ext}}$ (51 mg, quantitative) as a brown solid. ^1H NMR ($CDCl_3$, 400 MHz, 25°C): d = 8.69 (brd, *J* = 4.0Hz, 4H), 8.62-8.56 (m, 4H), 8.54-8.48 (m, 4H), 8.30 (s, 1.33H), 8.20 (s, 0.67H), 7.85 (dd, *J* = 7.7, 7.7Hz, 4H), 7.56 (d, *J* = 8.1Hz, 4H), 7.48-7.44 (m, 4H), 7.37-7.32 (m, 4H), 7.05-6.64 (m, 12H), 5.64 and 5.62 (2x s, 4H, isomers), 4.44-4.23 (m, 4H), 4.24-3.51 (m, 48H), 3.49-3.26 (m, 4H), 2.76 (t, *J* = 7.2Hz, 2.67H), 2.65 (t, *J* = 7.0Hz, 1.33H), 1.90-1.66 (m, 8H), 1.49-1.34 (m, 8H); ^{13}C NMR ($CDCl_3$, 125 MHz, 25°C): d = 155.8, 155.6, 151.0, 149.4, 149.2, 149.0, 147.7, 145.3, 145.0, 137.1, 132.9, 132.3, 129.6, 128.2, 128.0, 126.3, 124.3, 124.1, 122.9, 121.7, 121.4, 118.0, 114.4, 114.3, 92.7, 88.9, 71.4, 71.3, 71.0, 70.8, 70.7, 70.6, 70.0, 69.9, 69.8, 69.6, 69.5, 69.4, 68.2, 65.2, 57.0, 37.6, 27.0, 25.4, 25.0, 23.0, 22.9, 21.5; ESI-MS: m/z calcd for $C_{116}H_{134}N_{14}O_{16}P_4F_{24}$: 1134.469 $[M-2PF_6]^{2+}$, found: 1134.766.



bis-2,2':6,2?-terpyridine methylated rotaxane ($\mathbf{1}^{\mathit{cont}}$). A solution of rotaxane $\mathbf{1}^{\mathit{ext}}$ (64 mg, 22.8 µmol) in chloroform (10 mL) was washed with an aqueous solution of NaOH 1M (10 mL). The organic phase was dried over Na_2SO_4 and then evaporated in vacuo to provide compound $\mathbf{1}^{\mathit{cont}}$ (55 mg, quantitative) as a brown solid. As expected, the compound is obtained as a mixture of isomers *(1)*, and only major isomer is described. ^{1}H NMR ($CDCl_3$, 500 MHz, 25°C): d = 8.66 (brd, *J* = 3.6Hz, 4H), 8.56 (brd, *J* = 7.8Hz, 6H), 8.49 (s, 4H), 7.83 (ddd, *J* = 7.7, 7.7, 1.5Hz, 4H), 7.54 (d, *J* = 7.8Hz, 4H), 7.47 (d, *J* = 7.6Hz, 4H), 7.33-7.31 (m, 4H), 7.01-6.62 (m, 14H), 5.67 (s, 4H), 4.40-4.28 (m, 4H), 4.22-3.97 (m, 18H), 3.90-3.52 (m, 30H), 3.47-3.29 (m, 4H), 2.76 (brs, 4H), 1.88-1.55 (m, 8H), 1.50-1.33 (m, 8H); ^{13}C NMR ($CDCl_3$, 125 MHz, 25°C): d = 155.6, 155.6, 155.4, 150.5, 149.2, 148.9, 148.7, 148.7, 148.5, 144.7, 136.9, 132.7, 132.3, 129.4, 128.4, 124.1, 123.8, 122.7, 121.7, 121.2, 121.2, 178.3, 114.5, 114.4, 111.9, 92.6, 88.7, 72.7, 70.7, 70.6, 70.5, 70.2, 69.6, 69.5, 69.4, 69.3, 69.1, 68.6, 64.8, 56.6, 49.0, 37.5, 27.0, 25.3, 24.9, 22.7, 21.5; MALDI-TOF: calcd for $C_{116}H_{132}N_{14}O_{16}P_2F_{12}$: 988.497 $[M-2PF_6]^{2+}$, found: 988.597.

Procedures for polymerization of terpyridine rotaxanes

Contracted polymers: A solution of $FeCl_2$ (3.2 mg, 25.0 × 10^{-3} mmol, 1.0 equiv.) in CD_3CN (1250 µL) was added rotaxane monomer $\mathbf{1}^{cont}$ (56.7 mg, 25.0 × 10^{-3} mmol, 1.0 equiv.) in $CDCl_3$ (1250 µL). Immediately the colorless solution turned to purple and the mixture was stirred for 30 min at room temperature prior to further analyzes.

A solution of $Zn(OTf)_2$ (9.1 mg, 25.0 × 10^{-3} mmol, 1.0 equiv.) in CD_3CN (1250 µL) was added rotaxane monomer $\mathbf{1}^{cont}$ (56.7 mg, 25.0 × 10^{-3} mmol, 1.0 equiv.) in $CDCl_3$ (1250 µL). The colorless solution was stirred for 30 min at room temperature prior to further analyzes.

Extended polymers: A solution of $FeCl_2$ (3.2 mg, 25.0 × 10^{-3} mmol, 1.0 equiv.) in CD_3CN (1250 µL) was added rotaxane monomer $\mathbf{1}^{ext}$ (64.0 mg, 25.0 × 10^{-3} mmol, 1.0 equiv.) in $CDCl_3$ (1250 µL). Immediately the colorless solution turned to purple and the mixture was stirred for 30 min at room temperature prior to further analyzes.

A solution of $Zn(OTf)_2$ (9.1 mg, 25.0 × 10^{-3} mmol, 1.0 equiv.) in CD_3CN (1250 µL) was added rotaxane monomer $\mathbf{1}^{ext}$ (64.0 mg, 25.0 × 10^{-3} mmol, 1.0 equiv.) in $CDCl_3$ (1250 µL). The colorless solution was stirred for 30 min at room temperature prior to further analyzes.

Supplementary ^{1}H NMR experiments

Procedures for acido-basic titrations of monomers **1**$^{\mathbf{ext}}$ *and* **1**$^{\mathbf{cont}}$

Basic titration: A solution of **1**$^{\mathbf{ext}}$ (4×10^{-3} mmol) in $CDCl_3$ and a solution of NaOD (0.2 mol/L) in D_2O were prepared separately. 2μL of NaOD solution was added to the **1**$^{\mathbf{ext}}$ solution for each titration. The complete titration was finished after 22 times (up to 2.2 equiv.).

Acidic titration: A solution of **1**$^{\mathbf{cont}}$ (4×10^{-3} mmol) in $CDCl_3$ and of *d*-TFA (0.2 mol/L) in $CDCl_3$ were prepared separately. 2μL of *d*-TFA solution was added to the **1**$^{\mathbf{cont}}$ solution for each titration. The complete titration was finished after 22 times (up to 2.2 equiv.). Finally, the solution was washed with $NaPF_6$ (sat.) aqueous solution to perform a micro-exchange counter ion process.

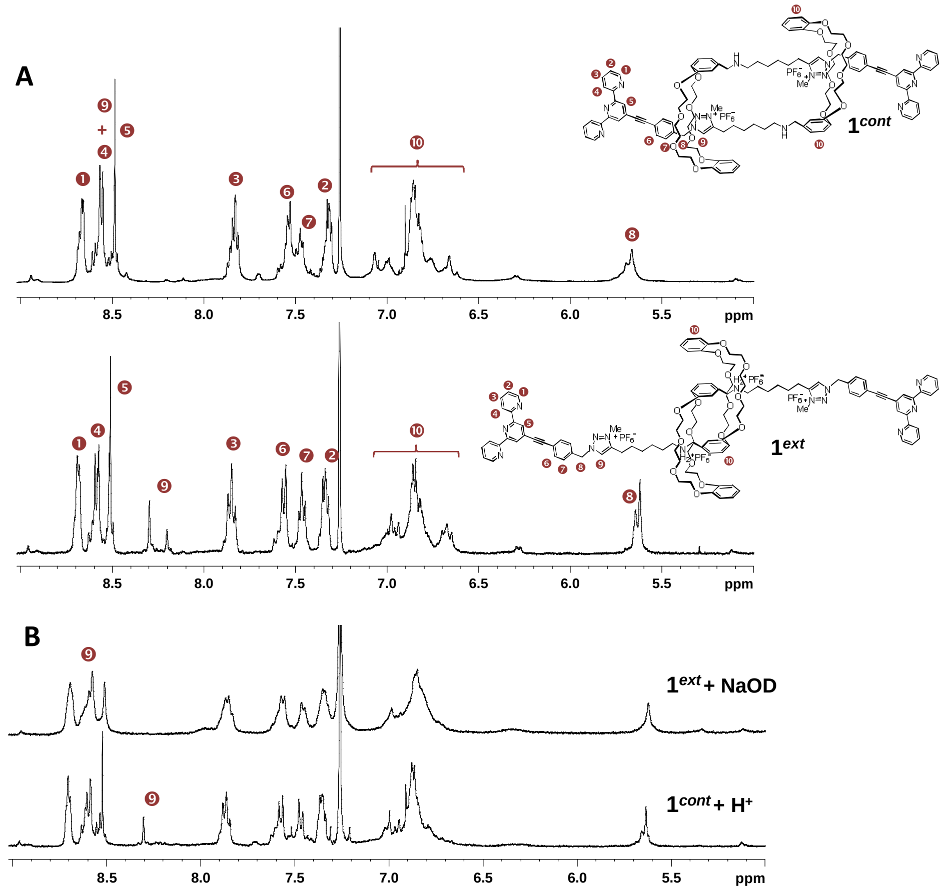


Fig. S1. (**A**) Characteristic ^{1}H NMR shifts of the imidazolium proton *number 9* in compounds **1**^{cont} and **1**^{ext}, together with (**B**) the superimposed spectra of **1**^{ext} + 2.2 eq. NaOD (leading to **1**^{cont}), and **1**^{cont} + 2.2 eq. *d*-TFA (leading to **1**^{ext}).

Supplementary UV-Vis experiments

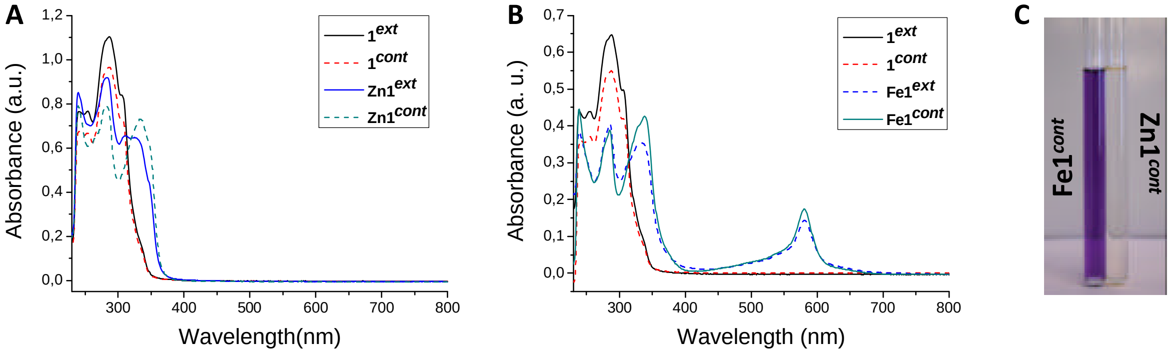


Fig. S2. UV-Vis spectra comparison between monomers **1**^{ext} / **1**^{cont} and (**A**) polymers **Zn1**^{ext} / **Zn1**^{cont} (2.10^{-2} mM in 1:1 $CDCl_3/CD_3CN$) and (**B**) polymers **Fe1**^{ext} / **Fe1**^{cont} (1.10^{-2} mM in 1:1 $CDCl_3/CD_3CN$); (**C**) Image of two polymer solutions (**Fe1**^{cont} and **Zn1**^{cont}) at a concentration of 10 mM in a 1:1 $CDCl_3/CD_3CN$ solvent mixture.

Supplementary scattering experiments

Neutron Scattering Experiments:

SANS experiments were carried out on the Pace spectrometer in the Léon Brillouin Laboratory at Saclay (LLB, France). The chosen incident wavelength, λ, depends on the set of experiments, as follows. For a given wavelength, the range of the amplitude of the transfer wave vector *q* was selected by changing the detector distance, D. Two sets of sample-to-detector distances and wavelengths were chosen (*D* = 1.2 m, l = 5 ± 0.5 Å; and *D* = 4.7 m, l = 8± 0.5 Å) so that the following *q*-ranges were respectively available: $3.54\times10^{-2} \leq q$ (Å^{-1}) $\leq 3.65\times10^{-1}$, and $5.2\times10^{-3} \leq q$ (Å^{-1}) $\leq 5.5\times10^{-2}$. Measured intensities were calibrated to absolute values (cm^{-1}) using normalization by the attenuated direct beam classical method. Standard procedures to correct the data for the transmission, detector efficiency, and backgrounds (solvent, empty cell, electronic, and neutronic background) were carried out. The scattered wave vector, *q*, is defined by equation 1, where q is the scattering angle:

$$q = \frac{4p}{l}\sin\frac{q}{2} \qquad \text{(eq. S1)}$$

The usual equation for absolute neutron scattering combines the intraparticle scattering $S_1(q) = V_{chain}\phi_{vol}P(q)$ form factor with the interparticle scattering $S_2(q)$ factor

$$I(q)(cm^{-1}) = (\Delta r)^2\left(S_1(q) + S_2(q)\right) = (\Delta r)^2\left(V_{chain} f_{vol} P(q) + S_2(q)\right) \qquad \text{(eq. S2)}$$

where $(\Delta\rho)^2 = (\rho_{monomer} - \rho_{solvent})^2$ is a contrast per unit volume between the polymer and the solvent and was determined from the known chemical composition. $\rho = \Sigma n_i b_i / (\Sigma n_i m_i v \times 1.66\times10^{-24})$ represents the scattering length per unit volume, b_i is the neutron scattering length of the species i, m_i the mass of species i, and *v* the specific volume of the monomer (which was measured and been taken to be equal to 0.704 cm^{3}g^{-1}) or the solvent (i.e., 0.77 cm^{3}g^{-1} for 50/50 $CDCl_3/CD_3CN$). P(*q*) is the form factor, $V_{chain} = Nvm \times 1.66\times10^{-24}$ is the volume of the N monomers (of mass m) in a chain and ϕ_{vol} is the volume fraction of monomer. In the high q-range, the scattering is assumed to arise from isolated chains; i.e., $S_2(q) = 0$, and thus $I(q) \propto P(q)$.

Dynamic and Static Light Scattering Experiments:

In the dynamic light scattering experiments (DLS), the normalized time autocorrelation function, $g^{(2)}(q,t)$, is measured as a function of the scattered wave-vector, q, given by $q=(4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index of the solvent (1.39 for 50/50 $CDCl_3/CD_3CN$ at 20 °C), and θ is the scattering angle. In our experiments, θ was varied between 30° and 140°, which corresponds to scattering wave vectors, q, in the range from 7.2×10^{-3} to 2.6×10^{-2} nm^{-1}. The measurements used a 3D DLS spectrometer (LS Instruments, Fribourg, Swiss) equipped with a 25mW HeNe laser (JDS uniphase) operating at λ=632.8 nm, a two channel multiple tau correlator (1088 channels in autocorrelation), a variable-angle detection system, and a temperature-controlled index matching vat (LS Instruments). The scattering spectrum was measured using two single mode fibre detections and two high sensitivity APD detectors (Perkin Elmer, model SPCM-AQR-13-FC). Solutions were filtered through 0.2 µm PTFE Millipore filter into the cylindrical scattering cell.

In Static Light Scattering (SLS) experiments, the excess of scattered intensity is measured with respect to the solvent. The absolute scattering intensity (i.e., the excess Rayleigh ratio in cm^{-1}) can be deduced by using a toluene sample reference for which the excess Rayleigh ratio is well-known ($R_{toluene}=1.3522\times10^{-5}$ cm^{-1} at 633 nm):

$$R_{solute}(cm^{-1}) = \frac{I_{solution} - I_{solvent}}{I_{toluene}} \times \left(\frac{n}{n_{toluene}}\right)^2 \times R_{toluene}(cm^{-1}) \qquad \text{(eq. S3)}$$

The usual equation for absolute light scattering combines the form factor P(q), the structure factor S(q) and the weight-average molecular weight M_W of the scattered objects:

$$R(q) = \frac{4p^2 n^2}{N_A l^4}\left(\frac{dn}{dc}\right)^2 CM_W P(q)S(q) \qquad \text{(eq. S4)}$$

C is the solute concentration in g/cm^3. The scattering constant is $K=4\pi^2 n^2 (dn/dC)^2/N_A\lambda^4$ where dn/dC is the refractive index increment (measured using a Mettler Toledo PortableLab refractometer) and N_A is Avogadro's number (K=3.23x10^{-8}, 5.54x10^{-6}, and 3.53x10^{-6} cm^2.g^{-2}.mol respectively for **Zn1**$^{\mathit{cont}}$, **Fe1**$^{\mathit{cont}}$, and **Fe1**$^{\mathit{ext}}$).

In DLS the experimental signal is the normalized time autocorrelation function of the scattered intensity:

$$g^{(2)}(q,t) = \frac{\langle I(q,0)I(q,t)\rangle}{\langle I(q,0)\rangle^2} \qquad \text{(eq. S5)}$$

The latter can be expressed in terms of the field autocorrelation function or equivalently in terms of the autocorrelation function of the concentration fluctuations, $g^{(1)}(q,t)$, through:

$$g^{(2)}(q,t) - 1 = a + b\left|g^{(1)}(q,t)\right|^2 \qquad \text{(eq. S6)}$$

Where α is the baseline (varying between 1×10^{-4} and 2×10^{-4} depending on the scattering angle and/or the system) and β the coherence factor, which in our experiments is varying between 0.7 and 0.9 depending on the samples. The normalized dynamical correlation function, $g^{(1)}(q,t)$, of polymer concentration fluctuations is defined as:

$$g^{(1)}(q,t) = \frac{\langle dc(q,0)dc(q,t)\rangle}{\langle dc(q,0)^2\rangle} \qquad \text{(eq. S7)}$$

Where $\delta c(q,t)$ and $\delta c(q,0)$ represent fluctuations of the polymer concentration at time t and zero, respectively.

In our experiments, some of our solutions were characterized by a single relaxation mechanism with a characteristic relaxation time inversely proportional to q^2. The extrapolation of $(\tau_c q^2)^{-1}$ to q=0, where τ_c is the average relaxation time of $g^{(1)}(q,t)$, yields the mutual diffusion coefficient D. The latter is related to the average apparent hydrodynamic radius, R_H, of the species through the Stokes-Einstein relation:

$$D = \frac{k_B T}{6\pi \eta_s R_H} \qquad \text{(eq. S8)}$$

Where k_B is the Boltzmann constant, η_s the solvent viscosity (0.444 cP for 50/50 $CDCl_3/CD_3CN$ at T=20°C), and T the absolute temperature.

To determine the sizes as well as the size distributions, especially when solutions were characterized by several relaxation mechanisms (e.g. monomers and polymers), we have used the Contin method based on the inverse Laplace transform of $g^{(1)}(q,t)$. If the spectral profile of the scattered light can be described by a multi-Lorentzian curve, then $g^{(1)}(q,t)$ can be written as:

$$g^{(1)}(q,t) = \int_0^\infty G(\Gamma)\exp(-\Gamma t)d\Gamma \qquad \text{(eq. S9)}$$

Where $G(\Gamma)$ is the normalized decay constant distribution.

Worm-like chain model:

To interpret the scattering and extract the structural parameters, it is also very useful to have a correct expression of the scattering of an individual chain, P(q). We have used an expression *(4, 5)* based on the expressions derived by Burchard and Kajiwara for rodlike structure *(6)* in which the form factor calculated by Sharp and Bloomfield *(7)* for finite wormlike chains of contour length L_c is used at low q.

$$P(q) = \left(\frac{2[\exp(-x) + x - 1]}{x^2} + \left[\frac{4}{15} + \frac{7}{15x} - \left(\frac{11}{15} + \frac{7}{15x} \right) \exp(-x) \right] \frac{2L_p}{L_c} \right) \times \exp\left[-\left(\frac{2qL_p}{\alpha} \right)^{\beta} \right] \qquad \text{(eq. S10)}$$
$$+ \left(\frac{1}{2L_c L_p q^2} + \frac{\pi}{qL_c} \right) \times \left(1 - \exp\left[-\left(\frac{2qL_p}{\alpha} \right)^{\beta} \right] \right)$$

With $x=L_cL_pq^2/3$ and valid for $L_c>4L_p$. Values of the empirical parameters $\alpha=5.53$ and $\beta=5.33$, which contribute to the balance between the low-q and large-q terms, have been optimized in ref. 4. Polydispersity and excluded volume effects can be neglected in the regime $qR_G>1$ where the scattering experiments were performed *(ref. 25 of the main text)*; with R_G being the radius of gyration of the chains.

High-q data can be fitted by a Guinier expression for the form factor of the polymer section:

$$V_{chain}P(q) = \frac{pS}{q}\exp\left(-\frac{q^2R_c^2}{2}\right) \qquad \text{(eq. S11)}$$

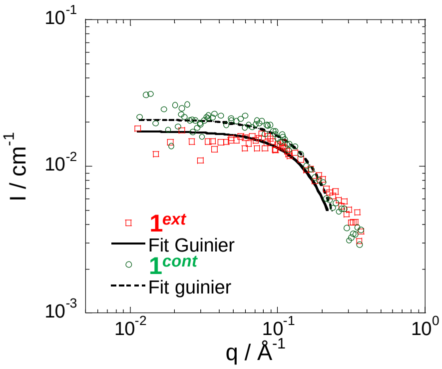


Fig. S3. SANS data for solutions of $\mathbf{1}^{ext}$ and $\mathbf{1}^{cont}$ (10 mM in 1:1 $CDCl_3/CD_3CN$ at T=20°C). The dashed lines represent the best fits of the data obtained using a classical Guinier expression (see eq. S14)

To determine the density *d* of the compounds we used the SANS measurements of the monomer solutions (without metals) as shown in Fig. S3. Indeed the scattering intensity extrapolated to q=0 can be expressed as follows:

$$I_0 = \frac{f\Delta r^2 M^{\circ}}{dN_a} = \frac{C\Delta r^2 M^{\circ 2}}{d^2N_a} \qquad \text{(eq. S12)}$$

With C being the monomer concentration, ? ?^{2}=(?-?$_{solvent}$)^2 the contrast term, M° the molar mass of the monomer, N_a the Avogadro number and *d* the density.

As the density is also present in the calculation of the contrast term we have to determine *d* which satisfies the following relation:

$$\frac{d^2}{\Delta r^2} = \frac{CM^{\circ 2}}{I_0 N_a} \qquad \text{(eq. S13)}$$

Hence, the extrapolation of the intensities to q=0 gives I_0=0.0185cm^{-1} for **1**$^{\mathbf{\mathit{ext}}}$ and I_0=0.021 cm^{-1} for **1**$^{\mathbf{\mathit{cont}}}$. Using these values and the relation S13 we thus obtained a density of 1.42g/cm^3 and 1.30 g/cm^3 for respectively **1**$^{\mathbf{\mathit{ext}}}$ and **1**$^{\mathbf{\mathit{cont}}}$.

Finally we can also determine the radius of gyration R_g of the monomers using the Guinier relation:

$$I(q) = I_0 \exp\left(\frac{-q^2 R_g{}^2}{3}\right) \qquad \text{(eq. S14)}$$

We obtained R_g=8.9+/-0.1Å for both monomers.

Table S1: Values of key parameters used in this study and determined from SANS on monomers **1**$^{\mathbf{\mathit{ext}}}$ and **1**$^{\mathbf{\mathit{cont}}}$ (solutions in 1:1 $CDCl_3/CD_3CN$ at T=20°C). *n.b. Here the M^O term is different from Table 1 because it does not include metal ions in the monomeric form.*

	C (mM)	**M° (g/mol)**	**I_0 (cm^{-1})**	**R_g (nm)**	$\frac{CM^{\circ 2}}{I_0 N_a}$ **(x10^{-21} g^2/cm^2)**	***d*** **(g/cm^3)**	**Scattering length density (x 10^{10}cm^{-2})**	Dr^2 **(x 10^{20}cm^{-4})**
1$^{\mathbf{\mathit{ext}}}$	10	2560	0.0185	0.89+/-0.1	5.88	1.42+/-0.14	2.17	3.4596
1$^{\mathbf{\mathit{cont}}}$	10	2268	0.0210	0.89+/-0.1	5	1.30+/-0.13	1.99	4.1616

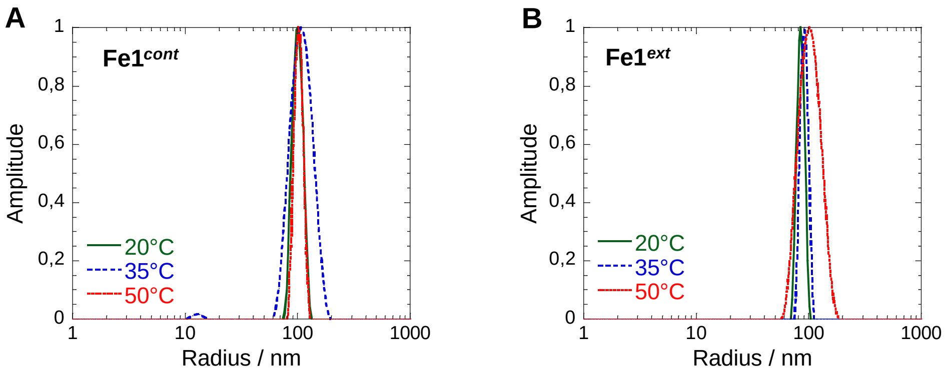


Fig. S4. Hydrodynamic radii (R_H) distribution obtained using the Contin method in DLS at θ=90° for (**A**) **Fe1**^{cont} and (**B**) **Fe1**^{ext} (in both case, c=10 mM in 1:1 $CDCl_3/CD_3CN$).

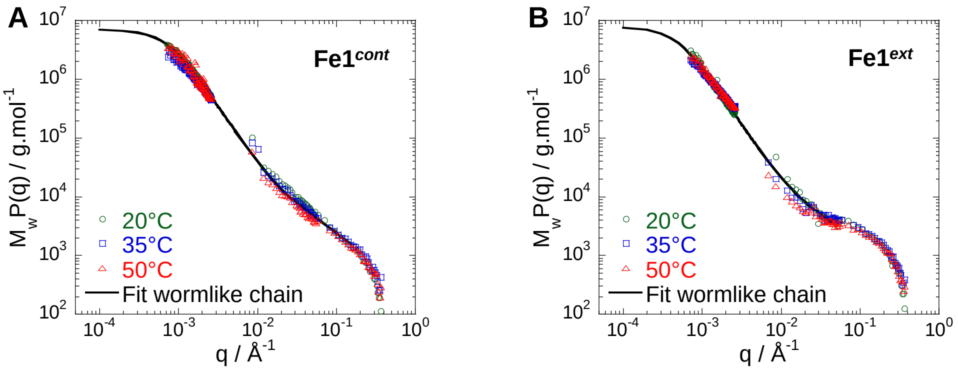


Fig. S5. Combined SLS and SANS measurements as a function of the temperature for solutions of (**A**) **Fe1**^{cont} and (**B**) **Fe1**^{ext} (10 mM in 1:1 $CDCl_3/CD_3CN$). The continuous line represents the data fit by the wormlike chain model (eq. S10).

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