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Synthesis of a soluble fullerene–rotaxane incorporating a furamide template

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Abstract—The synthesis of a fullerene–rotaxane is described. The thread is constituted by a C_{60} unit, which acts as a stopper, functionalized with a solubilizing side chain by 1,3 dipolar cycloaddition. The rotaxane is assembled by hydrogen bond-assisted synthesis using a fumaramide template.

1. Introduction

Rotaxanes have generated a lot of expectations due to their potential technological applications.[1,2] They can be prepared by means of different intermolecular interactions such as hydrogen bonds,[3–7] π-stacking,[8] metal complexation.[9] The applicability of these systems can be enhanced when using photo- and electroactive units like fullerenes. Owing to the unique photochemical and electrochemical properties of fullerene derivatives,[10,11] a wide variety of molecular devices can be produced with diverse applicability, including information storage, nanosensoring, conversion of light into electric current. C_{60} has shown a great efficiency as an electron acceptor in donor–acceptor systems.[10,11] Since photoinduced electron transfer between the donor and C_{60} can take place through space, they can be connected by means of non-covalent interactions. An example by Schuster and co-workers showed lifetimes up to 32 μs in ZnP–C_{60} Sauvage-type rotaxanes.[12,13] Nevertheless, it has been reported that interlocked ZnP–C_{60} dyads held together by hydrogen bonds have shown similar lifetimes to their covalently linked analogues.[14] The nature of the linker between the two units controls the distance, the orientation and the electronic coupling between the two units and thus, small structural variations can affect to the lifetime of the charge-separated state. This has been previously documented in covalently linked purpurin–C_{60} dyads.[15] Therefore, it is worthy to explore different interlocked systems not only to obtain higher lifetimes but also to understand which are the structural factors that control the efficiency of these systems.

In a collaborative work between Leigh's group and our group,[3] a fullerene–rotaxane was assembled by clipping a benzylic amide macrocycle around a fullerene thread via hydrogen bond-templated synthesis with a glycylglycine template. C_{60} acted both as a stopper and an electroactive unit. We decided to establish a straightforward synthetic route to fullerene–rotaxanes containing a fumaramide template that should establish the basis for the preparation of supramolecular donor–acceptor systems. Fumaramides have shown to be the best templates for closure of benzilic amide rotaxanes.[16] They can be photochemically isomerized leading to light driven molecular shuttles.[17–19]

2. Results and discussion

The target thread displayed two stoppers, C_{60} on one side and a 2,2′-diphenylethyl amide on the opposite side. These stoppers have been shown to cooperate in the stabilization of similar rotaxanes in the solid state by π-stacking.[16] More importantly, a fumaramide template was placed in between to direct the ring closure of the macrocycle around the thread.

Our synthetic strategy was based on the preparation of a fumaric acid derivative that contains the non-fullerenic stopper. Then, it could be coupled by amidation with a fullerene building block that displays a free amine (Scheme 1). Fumaric acid monoethyl ester **1** was coupled with 2, 2′-diphenylethylamine using the EDC/HOBt couple. The ethyl ester **2** was hydrolyzed in the presence of aqueous sodium hydroxide to yield the corresponding acid **3**.[18]

Keywords: Supramolecular; Fullerene; Rotaxane; Hydrogen bond.
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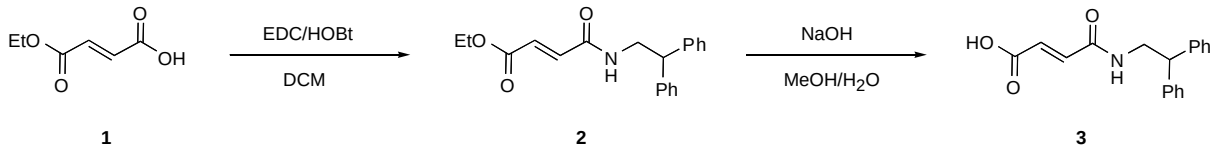
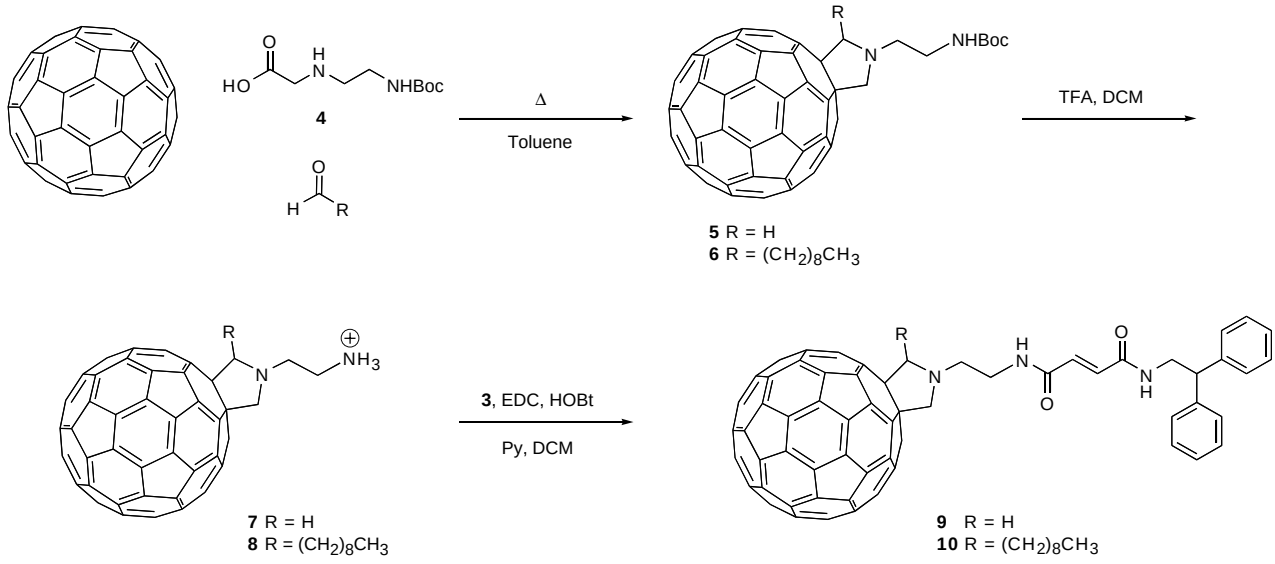


Scheme 1.

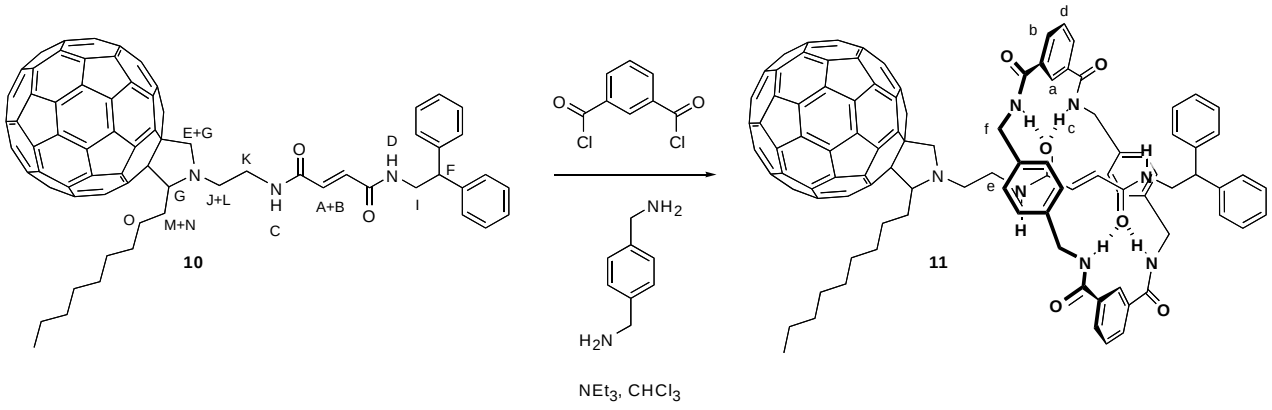
C_{60} was functionalized through [3+2] cycloaddition using an azomethine ylide generated in situ by condensation between aminoacid **4** and formaldehyde giving the monoadduct **5**, as previously reported by our group[20] (Scheme 2). Then, the amino group was deprotected yielding the ammonium salt **7**. The acid **3** was activated in the presence of EDC and HOBt and coupled with the fullerene salt **7** using pyridine as solvent, leading to the corresponding fullerene thread **9**. The thread **9** showed to be insoluble in chloroform or DMSO and could only be characterized by mass spectroscopy. The solubility of the thread in non-disrupting hydrogen bond solvents, such as chloroform, is one of the most important requirements for the preparation of this type of rotaxanes. However, rotaxane formation was attempted using thread **9** under the previously reported conditions,[3] but after the addition of the macrocycle precursors no reaction was observed.

These results clearly show that the combination of fullerenes and fumaramides gave highly insoluble molecules in chlorinated solvents. To overcome this problem, a solubilizing chain was introduced. This was easily achieved by functionalization of C_{60} using 1,3 dipolar cycloaddition (Scheme 2). The cycloaddition was carried out using again aminoacid **4**[20] and decanal instead of formaldehyde, introducing a hydrocarbon chain in the fulleropyrrolidine ring. This chain should increase the solubility in chloroform, but also should allow the clipping of the rotaxane since the hydrocarbon chain is pretty flexible. The reaction gave the fullerene building block **6**, which was deprotected using diluted TFA. The ammonium salt **8** was dissolved in pyridine and allowed to react with acid **3**, which was previously activated using the EDC/HOBt couple. The reaction afforded the desired thread **10**, which was soluble in chloroform and was fully characterized by NMR, MS, IR and UV–vis-NIR. A purity >98% was observed by HPLC using toluene/*i*PrOH 99:1 as eluent. The chromatogram showed a single peak corresponding to thread **10** with a retention time of 31 min.

Rotaxane **11** was assembled by slow addition of isophthaloyl chloride and *p*-xylylenediamine in the presence of NEt_3 (Scheme 3). It was purified by flash chromatography. The formation of the rotaxane **11** was confirmed both by NMR (^{1}H NMR, COSY) and MS. The purity of rotaxane **11** was checked by HPLC showing a single peak at 29 min and a purity >98%. The ^{1}H NMR spectrum of rotaxane **11** in $CDCl_3$ shows an upfield shift of the protons on the fumaramide double bond (from 6.88 to 5.74 ppm), which is more pronounced in pyridine-d_5 (from 7.76 to 6.22 ppm) (Figure 1, signals A and B). This effect proved not only the formation of the rotaxane but also that the macrocycle laid on the fumaramide template. The shifting observed is caused by the shielding of the benzylic aromatic rings on the macrocycle over the thread due to anisotropy. The spectrum of rotaxane **11** in $CDCl_3$ displays a shifting of the amide protons (Figure 1, signals C and D) to the aromatic region. This effect was observed more clearly in pyridine-d_5, where the amide protons on the thread **10** appeared more downfield (9.82 and 9.51 ppm) due to hydrogen bonding with the solvent. The spectrum of rotaxane **11** in pyridine-d_5 showed the amide protons of the template shifted even more downfield (10.72 and 10.53 ppm).



Scheme 2.



Scheme 3.

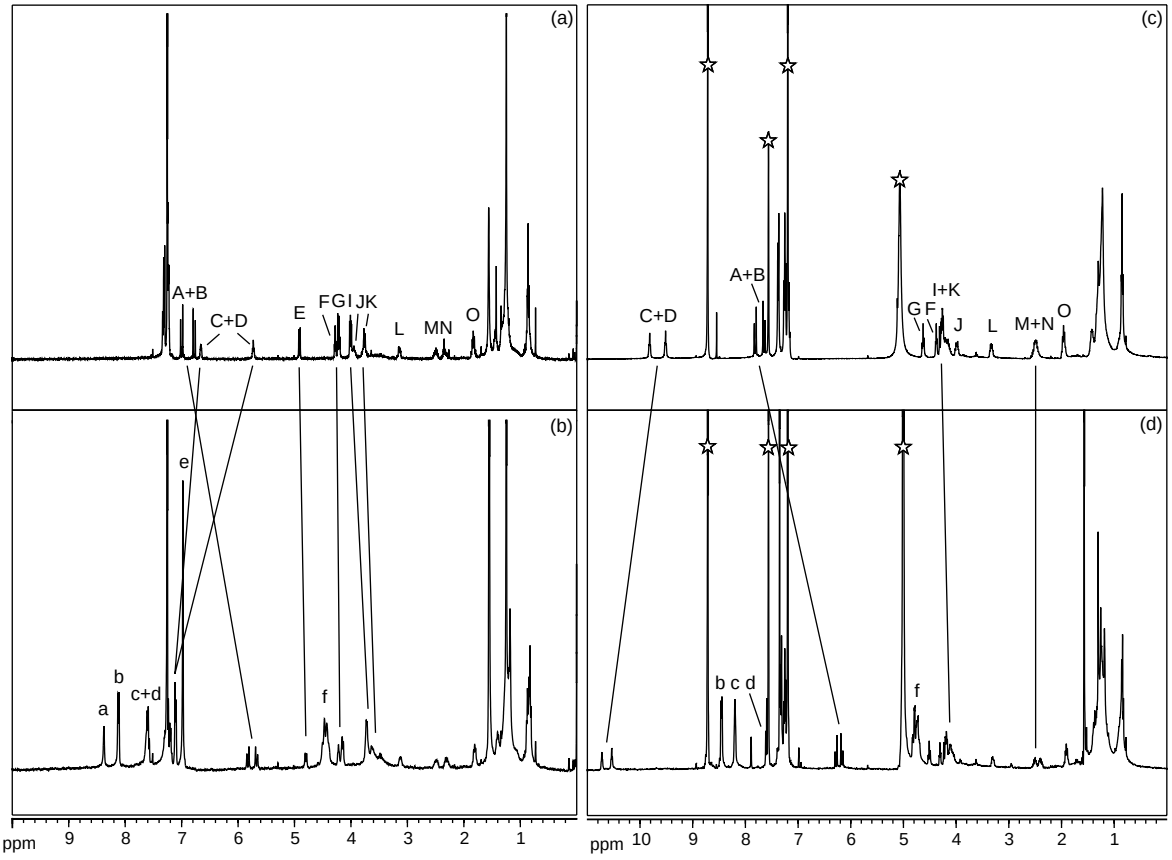


Figure 1. ^{1}H NMR (400 MHz) of (a) thread **10** in $CDCl_{3j}$, (b) rotaxane **11** in $CDCl_{3j}$, (c) thread **10** in pyridine-d_5 and (d) rotaxane **11** in pyridine-d_5. The peaks highlighted correspond to the residual solvent peaks.

On the other hand the UV–vis-NIR spectra of thread **10** and rotaxane **11** did not show any major differences.

3. Conclusions

Fullerene–rotaxane **11** was assembled by hydrogen bond-directed synthesis using a fumaramide template. The insolubility of the fumaramide template together with C_{60} was overcome by the introduction of a solubilizing hydrocarbon chain. This required the preparation of a novel fullerene building block by 1,3-dipolar cycloaddition. The solubilization of the new thread in chloroform allowed the preparation of the rotaxane.

4. Experimental

4.1. General

NMR spectra were recorded on a Varian Gemini-200 (200 MHz) or on a Jeol (400 MHz) at room temperature in $CDCl_3$ (unless otherwise stated). Chemical shifts reported in ppm are referred to TMS. 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. HPLC experiments were carried out using a semipreparative Phenomenex

Prodigy 5 μm silica 100 Å column and a Waters 996 photodiode detector. Toluene/*i*PrOH 99:1 was used as the mobile phase. Flow rate gradient 0–1 mL/min (0–3 min), followed by a constant flow rate of 1 mL/min (3–57 min). Commercially available products were used without further purification. Anhydrous $CHCl_3$ stabilized with amylenes was purchased from Aldrich and used as received.

4.1.1. Fumaric acid mono-2,2′-diphenylethylamide monoethyl ester (2). Fumaric acid monoethyl ester (200 mg, 1.39 mmol), 2,2′diphenylethylamine (274 mg, 1.39 mmol), HOBt (170 mg, 1.39 mmol) were stirred at room temperature in DCM (10 mL). EDC (275, 1.39 mmol) was added in small portions and the resulting solution was stirred at room temperature for 20 h. The solution was taken up with AcOEt (50 mL) and was washed with aqueous HCl (0.5 N, 50 mL), aqueous $NaHCO_3$ (saturated, 50 mL) and brine (50 mL). The organic phase was dried over $MgSO_4$ and the solvent was evaporated under vacuum yielding the desired product (423 mg, 93%).

Mp 111–112 °C (Mp 112–113 °C).[18] ^{1}H NMR (200 MHz): 7.34–7.19 (m, 10H, Ar), 6.77 (d, $J=14.4$ Hz, 1H, HC═CH), 6.72 (d, $J=14.4$ Hz, 1H, HC═CH), 5.80–5.65 (m, 1H, NH), 4.30–4.15 (m, 3H, OCOCH_2CH$_3$ and CHPh$_2$), 4.01 (dd, $J=8.0$, 5.7 Hz, OCNHCH_2), 1.31 (t, $J=7.0$ Hz, OCOCH$_2$CH_3).

4.1.2. Fullerene thread 9. Fullerene **7**[20] (25 mg, 27 μmol) was dissolved in pyridine (anhydrous, 2.5 mL). Then a solution of acid **3**[18] (16 mg, 54 μmol), EDC (11 mg, 54 μmol), HOBt (7 mg, 54 μmol) in CH_2Cl_2 (5 mL), which was previously stirred for 15 min, was added over the fullerene solution. The resulting solution was stirred at room temperature for 15 min. The solution was washed with aqueous HCl (0.5 N, 50 mL×2), aqueous $NaHCO_3$ (saturated, 50 mL×2) and brine (50 mL). The organic phase was dried over $MgSO_4$ and the solvent was evaporated under vacuum. The crude was purified by flash chromatography (toluene/*i*PrOH 8:2) and by reprecipitation ($CHCl_3$/MeOH 9:1/ether) yielding the desired product (25 mg, 85%). MS: 1086 $(M+H)^+$.

4.1.3. Fullerene building block 6. A solution of C_{60} (237 mg, 0.312 mmol), aminoacid **4**[20] (50 mg, 0.313 mmol) and decanal (244 mg, 1.560 mmol) were sonicated for 30 min in toluene (240 mL). Then the solution was refluxed for 25 min. The solvent was evaporated by vacuum distillation. The residue was purified by flash chromatography (toluene), unreacted C_{60} was eluted followed by the desired product. This was further purified by reprecipitation using $CHCl_3$/MeOH (120 mg, 37%).

^{1}H NMR (200 MHz): 5.29 (br s, 1H, NH); 4.96 (d, 1H, $J=10.4$ Hz, C_{60}–CH_2–N); 4.34 (d, 1H, $J=5.8$ Hz, C_{60}–CHR–N); 4.27 (d, 1H, $J=10.4$ Hz, C_{60}–CH_2–N); 3.82–3.55 (m, 3H, NCH_2CH_aH$_b$N); 3.18–3.12 (m, 1H, NCH$_2$CH$_a$$H_b$N); 2.62–2.25 (m, 2H, C_{60}–CH–CH_2); 2.00–0.85 (m, 26H). ^{13}C NMR (50 MHz): 156.15, 155.98, 154.80, 153.34, 147.04, 147.02, 146.37, 146.35, 146.13, 146.11, 146.03, 145.92, 145.88, 145.85, 145.83, 145.55, 145.53, 145.42, 145.22, 145.16, 145.14, 145.12, 145.05, 144.55, 144.41, 144.30, 144.28, 143.08, 142.97, 142.53, 142.52, 142.49, 142.12, 142.08, 142.06, 142.03, 141.99, 141.96, 141.95, 141.91, 141.69, 141.63, 141.13, 140.09, 139.80, 139.55, 136.78, 136.01, 135.40, 135.32, 77.25, 76.51, 66.48, 51.70, 31.91, 31.48, 30.15, 29.70, 29.58, 29.30, 28.52, 27.60, 22.72, 14.19. IR (NaCl): 3356, 2922, 2849, 1701, 1498, 1461, 1363, 1248, 1168. MS: 1034 $(M+H)^+$.

4.1.4. Fullerene thread 10. Fullerene **6** (120 mg, 0.116 mmol) was dissolved in DCM (3 mL) and TFA (3 mL) was added in small portions. The resulting solution was stirred at room temperature for 3 h. The solvent was evaporated under vacuum. The residue was then dissolved in pyridine (anhydrous, 12 mL). Then a solution of acid **3**[18] (51 mg, 0.172 mmol), EDC (36 mg, 0.172 mmol), HOBt (25 mg, 0.182 mmol) in DCM (12 mL), which was previously stirred for 15 min, was added to the fullerene solution. The resulting solution was stirred at room temperature for 15 min. The solution was washed with aqueous HCl (0.5 N, 50 mL×2), aqueous $NaHCO_3$ (saturated, 50 mL×2) and brine (50 mL). The organic phase was dried over $MgSO_4$ and the solvent was evaporated under vacuum. The crude was purified by flash chromatography ($CHCl_3$) yielding the desired product (117 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$): 7.4–7.2 (m, 10H, Ar); 6.99 (d, 1H, $J=14.82$ Hz, CH═CH); 6.77 (d, 1H, $J=14.82$ Hz, CH═CH); 6.70–6.60 (m, 1H, CONH); 5.73 (t, 1H, $J=5.88$ Hz, CONH); 4.90 (d, 1H, $J=10.25$ Hz, H_E); 4.28 (t, 1H, $J=6.63$ Hz, CH_FPh$_2$); 4.25–4.15 (m, 2H, H_G); 4.00 (dd, 2H, $J=5.89$, 7.76 Hz, H_I); 3.97–3.90 (m, 1H, H_J); 3.75–3.60 (m, 2H, H_K); 3.20–3.10 (m, 1H, H_L); 2.55–2.45 (m, 1H, H_M); 2.45–2.35 (m, 1H, H_N); 1.83 (q, 2H, $J=7.85$ Hz, H_O); 1.7–0.8 (m, 17H). ^{1}H NMR (400 MHz, pyridine-d_5): 9.82 (t, 1H, $J=5.59$ Hz, CONH); 9.51 (t, 1H, $J=5.62$ Hz, CONH); 7.88 (d, 1H $J=14.98$ Hz, CH═CH); 7.64 (d, 1H, $J=14.98$ Hz, CH═CH); 7.50–7.10 (m, 10H, Ar); 4.62 (t, 2H, H_G); 4.38 (t, 1H, $J=5.58$ Hz, CH_FPh$_2$); 4.30–4.10 (m, 4H, H_I+H_K); 4.05–3.90 (m, 1H, m, 1H, H_J); 3.40–3.25 (m, 1H, m, 1H, H_L); 2.60–2.40 (m, 2H, H_M+H_N); 1.96 (q, 2H, $J=7.60$ Hz, H_O); 1.5–0.6 (m, 17H). ^{13}C NMR (50 MHz, pyridine-d_5): 165.74, 165.62, 157.49, 156.04, 154.77, 147.69, 147.66, 147.42, 147.35, 147.07, 146.83, 146.78, 146.73, 146.71, 146.58, 146.55, 146.51, 146.48, 146.34, 146.25, 145.93, 145.89, 145.83, 145.77, 145.73, 145.31, 145.14, 145.04, 145.01, 143.82, 143.66, 143.20, 142.95, 142.92, 142.76, 142.69, 142.65, 142.58, 142.41, 142.35, 140.74, 140.70, 140.46, 140.25, 137.76, 134.93, 134.35, 134.22, 129.42, 129.05, 127.37, 77.50, 72.39, 51.70, 32.65, 30.91, 30.55, 30.39, 30.35, 30.12, 28.14, 23.54, 14.87. IR (NaCl): 3745, 3288, 3079, 2921, 2850, 2360, 1630, 1544, 1456, 1338, 1189, 748. MS: 1212 $(M+H)^+$. UV–vis-NIR (THF, λ_{max}): 255, 292, 320, 431, 704.

4.1.5. Rotaxane 11. A solution of *p*-xylylenediamine (144 mg, 1.050 mmol) in $CHCl_3$ (anhydrous, 40 mL) and a separate solution of isophthaloyl chloride (213 mg, 1.050 mmol) in $CHCl_3$ (anhydrous, 40 mL) were added dropwise, simultaneously for 4 h to a stirred solution of the thread **10** (85 mg, 0.070 mmol) in $CHCl_3$ (anhydrous, 150 mL) containing NEt_3 (153 μL, 2.100 mmol) under argon. After the addition, the reaction mixture was stirred overnight at room temperature. The solution was filtered through Celite, concentrated to dryness and

chromatographed ($CHCl_3$), giving unreacted thread (33 mg) and rotaxane **11** (30 mg, 25% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 8.37 (s, 2H, H_a); 8.11 (d, 4H, J=8.30 Hz, H_b); 7.69–7.59 (m, 4H, NH_c); 7.59 (t, 2H, J=7.94 Hz, H_d); 7.30–7.20 (m, 10H, Ar); 7.70–7.10 (m, 2H, H_C+H_D); 6.98 (s, 8H, H_e); 5.82 (d, 1H, J=14.77 Hz, C*H*=CH); 5.67 (d, 1H, J=14.77 Hz, CH=C*H*); 4.80 (d, 1H, J=10.64 Hz, H_E); 4.55–4.35 (m, 8H, H_f); 4.22 (t, 1H, J=4.75 Hz, CH_FPh_2); 4.19–4.10 (m, 5H, $H_I+H_J+H_K$); 3.15–3.05 (m, 1H, H_L); 2.60–2.40 (m, 1H, H_M); 2.40–2.20 (m, 1H, H_N); 1.85–1.75 (m, 2H, H_O); 1.5–0.7 (m, 17H).

^{1}H NMR (400 MHz, pyridine-d_5): 10.75 (t, 1H, J=5.15 Hz, CON*H*); 10.53 (t, 1H, J=5.50 Hz, CON*H*); 8.45 (dt, 4H J=7.76 and 1.82 Hz, H_b); 8.25–8.15 (m, 4H, H_c); 7.59 (t, 2H, J=7.76 Hz, H_d); 7.40–7.15 (m, Ar); 6.28 (d, 1H, J=14.91 Hz, C*H*=CH); 6.17 (d, 1H, J=14.91 Hz, CH=C*H*); 4.85–4.60 (m, 8H, H_f), 4.51 (t, 2H, J=7.94 Hz, H_G); 4.31 (t, 1H, J=5.63 Hz, CH_FPh$_2$); 4.30–4.00 (m, 5H, H_I, H_K, H_J); 3.35–3.25 (m, 1H, H_L); 2.55–2.45 (m, 1H, H_M); 2.45–2.35 (m, 1H, H_N); 1.9 (q, 2H, J=7.96 Hz, H_O); 1.4–0.6 (m, 17H). IR (NaCl): 2360, 1639, 1525, 466. MS: 1744 $(M+H)^+$. UV–vis-NIR (THF, λ_{max}): 249, 292, 320, 431, 703.

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