Template Synthesis of Rotaxanes with Carbamate-Linked Axles

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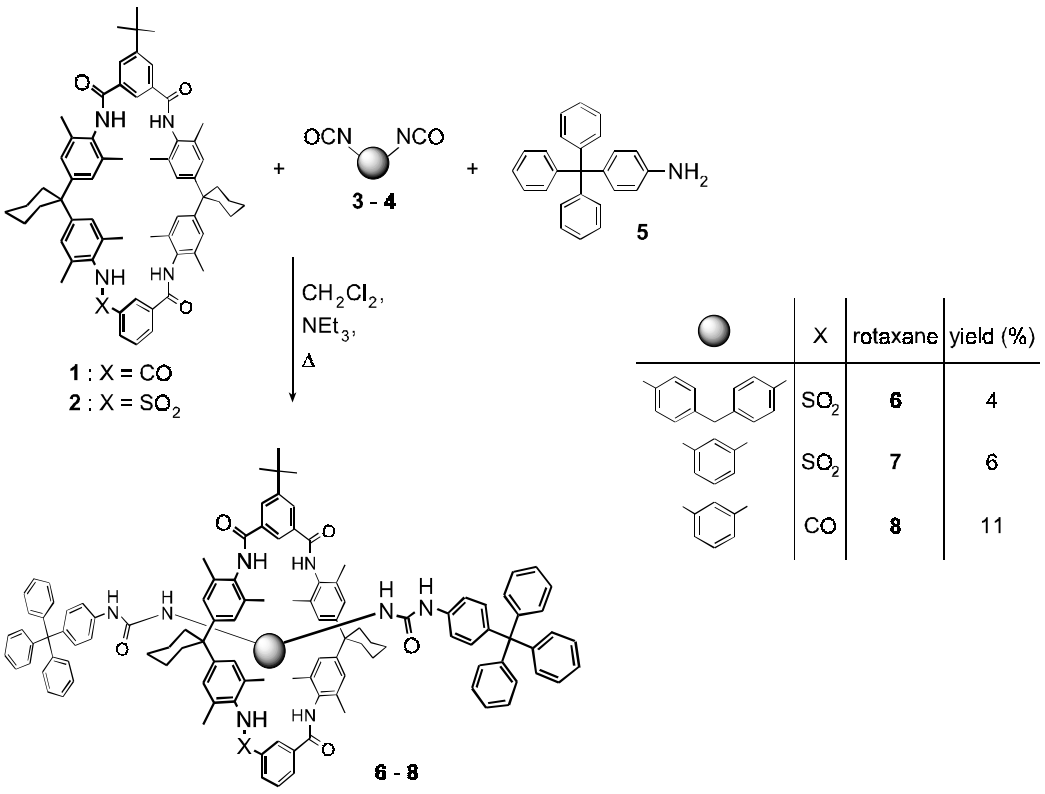
Abstract. Proceeding from diisocyanates **4** and **10**–**13**, (4-hydroxyphenyl)triphenylmethane **14** and tetralactame macrocycles **1**, **2** and **9** the threading synthesis of rotaxanes **16**–**21** containing carbamate units in the axle is described. In addition to aromatic diisocyanates aliphatic ones are firstly introduced as building blocks in rotaxane chemistry. The template synthesis of the new tetralactame macrocycle **9** with a pyridine unit is presented. It is used as wheel in a rotaxane synthesis towards the carbamate-linked rotaxane **21**.

Non-ionic template effects [1] proved to be a successful concept to synthesize supramolecular architectures [2], especially hydrogen bond-mediated catenane [3] and rotaxane [4] formation [5].

In the beginning aromatic diacid dichlorides were believed to be the guests to fit into tetralactame macrocycles. Reaction with bulky amine stoppers in the presence of a macrocycle led to amide-based rotaxanes. Yet by replacing the aromatic diacid dichloride "guests" with aliphatic ones it was even possible to synthesize amide-based rotaxanes with aliphatic building blocks [6]. So π-stacking seemed not to be necessary for rotaxane formation. In 1997 we were able to introduce diisocyanates [7] as building blocks. Treatment of macrocycles **1** [8] and **2** [9] with diisocyanates **3** and **4** and further reaction with bulky amine stoppers **5** led to rotaxanes **6**–**8** with urea-linked axles [10] in 4–11% yield (Scheme 1). First attempts to synthesize these rotaxanes at room temperature failed, so we raised the reaction temperature to 40 °C. Although a rise of temperature is weakening the hydrogen bonds [11] between macrocyclic amide host and carbonylic guest, we were able to cre-



	X	rotaxane	yield (%)
	SO_2	**6**	4
	SO_2	**7**	6
	CO	**8**	11

Scheme 1 Synthesis of rotaxanes containing urea-linked axles

  1436-9966/99/3410X-542 $ 17.50 + .50/0

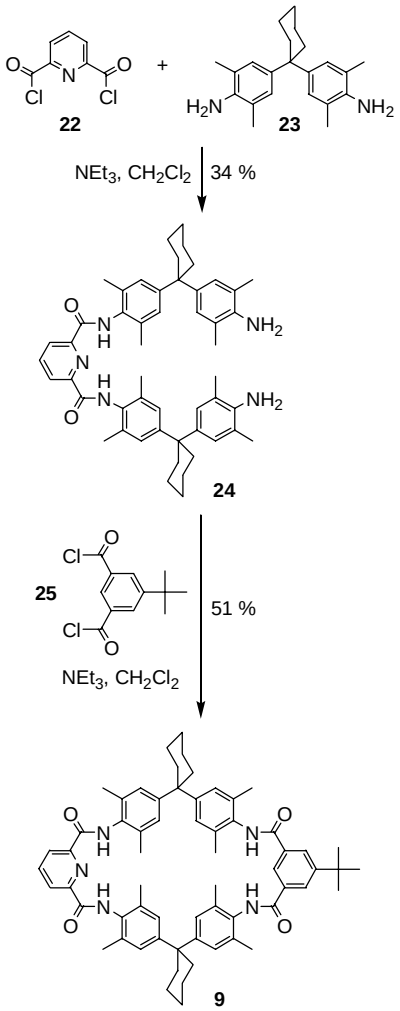
ate [2]rotaxanes with urea-linked axles by this trick.

Using the hydroxy stopper **14** instead of the amine stopper **5** we synthesized a hitherto unknown type of structure perfect [2]rotaxane containing a carbamate-linked axle [12]. A first synthesis led to carbamate rotaxane **15** in 24% yield [10].

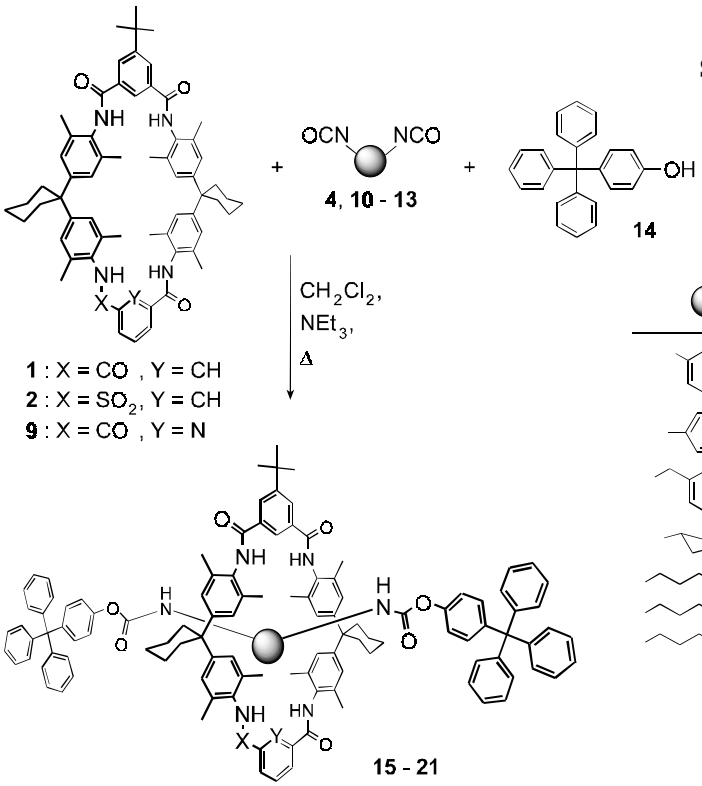
Results and Discussion

Applying the synthetic strategy which resulted in rotaxane **15** we were able to create the new carbamate-linked rotaxanes **16** and **17** in 9 and 6% yield containing aromatic units in the axle. Encouraged by these results we successfully introduced the aliphatic diisocyanates **12** and **13** as building blocks in rotaxane chemistry. Reaction with macrocycles **1** and **2** and stopper **14** led to the new rotaxanes **18**–**20** in 10–23% yield. A higher yield of 28% could be obtained by using the yet unpublished macrocycle **9** containing a pyridino unit leading to rotaxane **21** (Scheme 2).

The preparation of this new macrocycle **9** was carried out according to macrocycles **1** [8] and **2** [9]. Reaction of 2,6-pyridine dicarboxylic acid dichloride **22** with diamine **23** [13] led to diamide **24** [14] in 34% yield. The following ring closure with 5-*t*-bu-isophthalic acid dichloride **25** produced macrocycle **9** [15] in 51% yield (Scheme 3).



Scheme 3 Synthesis of macrocycle **9**



	X	Y	rotaxane	yield (%)
	CO	CH	**15**	24
	CO	CH	**16**	9
	CO	CH	**17**	6
	CO	CH	**18**	23
	CO	CH	**19**	15
	SO_2	CH	**20**	10
	CO	N	**21**	28

Scheme 2 Synthesis of rotaxanes with carbamate-linked axles

Compared to the urea-linked rotaxanes the yields of carbamate-linked rotaxanes are slightly higher, although the hydroxy stopper displays a less nucleophilic character than the corresponding amine stopper. This phenomena can be explained by the creation of an intermediate phenolate anion, since recent results have shown that phenolate anions are selectively incorporated into tetralactame macrocycles [16].

Conclusions

The applied threading method described here led to a series of new rotaxanes containing carbamate-units in the axle. Even aliphatic axle building blocks could be integrated into these rotaxanes. A new macrocyclic wheel containing a pyridino building block was introduced, and its use resulted in the corresponding rotaxane in a relative high yield of 28%.

The rotaxanes presented here display a synthetic potential since the carbamate bonds in the axle can be hydrolysed without breaking open the amide bonds in the macrocycle. This may make it possible to control and study the dethreading process of these rotaxanes. Employment of glycols as hydroxy components together with diisocyanates and tetralactame macrocycles may lead to rotaxanes containing a polymeric carbamate backbone.

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Experimental

Chemicals were purchased from Merck, Aldrich and Lancaster. The diisocyanates were donated by Bayer AG. All chemicals were used as received. Dichloromethane was destilled prior use. Yields refer to chromatographically and spectroscopically homogeneous materials. All reactions were monitored by thin-layer chromatography (TLC) carried out on aluminium sheets precoated with silica gel 60 F_{254} (Merck 1.05554). The sheets were inspected by UV light (λ = 254 nm) as visualising agent. Column chromatography was carried out on silica gel 60 (Merck 15 101). Melting points were determined on a Kofler microscope heater (Reichert, Wien, Austria) and are not corrected. Microanalyses were performed by the microanalytical department at the Kekulé-Institut für Organische Chemie und Biochemie of the university of Bonn. MALDI-TOF mass-spectra were recorded on a Micromass Tof Spec E spectrometer (Micromass, Manchester, UK). The matrix used was 2,5-dihydroxybenzoic acid (DHB). The ^{1}H- and ^{13}C NMR spectra were obtained on a Bruker AM 250 (250 MHZ (^{1}H), 62.9 MHz (^{13}C)), a Bruker AM 400 (400 MHz (^{1}H), 100.6 MHz (^{13}C)) and a Bruker AM 500 (500 MHz (^{1}H), 125.8 MHz (^{13}C)) spectrometer in commercially available deuterated solvents (internal reference was the residual undeuterated solvent: $CHCl_3$ 7.24 ppm, DMSO 2.49 ppm, CH_3OH 3.35 and 4.78 ppm). The following abbreviations were used to indicate NMR-multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad).

N,N'-Bis{4-[1-(4-amino-3,5-dimethylphenyl)cyclohexyl]-2,6-dimethylphenyl}pyridine-2,6-diamide (**24**)

10.0 g (31 mmol) of diamine **23** were dissolved in a solution of 1.4 ml of triethylamine in 50 ml of dichloromethane. 2.0 g (10 mmol) of pyridine-2,6-dicarboxylic acid dichloride **22** were similarly dissolved in 100 ml of dichloromethane, the solution transferred to a dropping funnel, and then added dropwise to the diamine solution over a period of 4 h. The reaction mixture was stirred for further 5 h. The crude product was purified by column chromatography (chloroform/ethyl acetate 4:1). *m.p.* 134–135 °C, R_f = 0.1 (chloroform/ethyl acetate 4:1). Yield 2.6 g (34%). MALDI-TOF-MS: *m/z* = 798.9 $[M + Na]^+$. – ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ/ppm = 1.55 (br, 12H, aliph. CH_2), 2.14 (s, 12H, Ar–CH_3), 2.18 (s, 12H, Ar–CH_3), 2.20 (br, 8 H, aliph. CH_2), 3.45 (br, 4H, amine-NH), 6.87 (s, 4H, ar. H), 7.04 (s, 4H, ar. H), 8.04 (t, ^3J = 8.0 Hz, 1H, ar. H), 8.47 (d, ^3J = 8.0 Hz, 2H, ar. H), 9.38 (s, 2H, amide-NH). – ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ/ppm = 17.90, 18.64 (CH_3), 22.75, 26.23, 36.98 (CH_2), 125.22, 126.77, 137.45 (CH), 44.68, 121.15, 130.12, 134.20, 139.08, 139.89, 148.26 (C_q), 161.33, 171.22 (C=O).

11'(tert-Butyl)-5',17',23',35',38',40',43',45'-octamethyldispiro[cyclohexane-1,2'-[7,15,25,33,39]pentaazaheptacyclo [32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaen-20',1''-cyclohexane]-8',14',26',32'-tetrone (**9**)

1 000 mg (1.3 mmol) of diamide **24** were dissolved in a mixture of 0.4 ml of triethylamine in 200 ml of dichloromethane. In the same way 330 mg (1.3 mmol) of 5-*t*-bu-isophthalic acid dichloride **25** were dissolved in 200 ml of dichloromethane. Both sultions were simultaneously added to 1 200 ml of the same solvent over a period of 8 h. The crude product was purified by column chromatography (chloroform/ethyl acetate 6:1). *m.p.* > 300 °C, R_f = 0.5 (chloroform/ethyl acetate 6:1). Yield 642 mg (51%). MALDI-TOF-MS: *m/z* = 984.8 $[M + Na]^+$. – ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ/ppm = 1.42 (s, 9H, $C(CH_3)_3$), 1.51 (br, 4H, aliph. CH_2), 1.64 (br, 8H, aliph. CH_2), 2.18 (s, 12H, Ar–CH_3), 2.19 (s, 12H, Ar–CH_3), 2.26 (br, 8H, aliph. CH_2), 6.96 (s, 4H, ar. H), 6.97 (s, 4H, ar. H), 7.18 (s, 2H, amide–NH), 7.92 (s, 1H, ar. H), 8.14 (t, ^3J = 8.0 Hz, 1H, ar. H), 8.23 (s, 2H, ar. H), 8.49 (d, ^3J = 8.0 Hz, 2H, ar. H), 8.90 (s, 2H, amide–NH). – ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ/ppm = 18.92, 19.00, 31.22 (CH_3), 22.84, 26.29, 35.81 (CH_2), 122.70, 125.46, 126.56, 126.76, 129.01, 139.61 (CH), 35.37, 45.03, 130.36, 131.22, 134.50, 134.61, 134.83, 147.94, 148.51, 148.61, 154.19 (C_q), 161.21, 171.56 (C=O).

[2]{1,4-N,N'-Bis[carboxy(4-(triphenylmethyl)phenoxy)]-phenylene diamine}{11'-(tert-butyl)-5',17',23',35',38',40',43',45'-octamethyldispiro[cyclohexane-1,2'-[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]-hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,31(39),34,36,37,40,42,45]octadecaen-20',1''-cyclohexane]-8',14',26',32'-tetrone}rotaxane (**16**)

690 mg (0.72 mmol) of macrocycle **1** and 115 mg (0.72 mmol)

of 1,4-phenylene diisocyanate (**10**) were dissolved in 100 ml of dichloromethane. This solution was added to a refluxing solution of 504 mg (1.50 mmol) of (4-hydroxyphenyl)triphenylmethane (**14**) and a few drops of triethylamine in 100 ml of the same solvent over a period of 2h. The crude product was purified by column chromatography (dichloromethane/ethyl acetate 20:1). *m.p.* > 300 °C, R_f = 0.2 (dichloromethane/ethyl acetate 20:1). Yield 119 mg (9%). MALDI-TOF-MS: *m/z* = 1816.8 $[M + Na]^+$. – ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ/ppm = 1.31 (s, 9H, $C(CH_3)_3$), 1.51 (br, 4H, aliph. CH_2), 1.61 (br, 8H, aliph. CH_2), 2.15 (s, 24H, Ar–CH_3), 2.33 (br, 8H, aliph. CH_2), 6.51 (d, ^3J = 8.7 Hz, 2H, ar. H), 6.67 (d, ^3J = 8.7 Hz, 4H, ar. H), 6.90 (d, ^3J = 8.7 Hz, 4H, ar. H), 7.02 (s, 12H, ar. H), 7.10 – 7.35 (signal group, 27H, ar. H), 7.68 (t, ^3J = 8.7 Hz, 1H, ar. H), 8.03 (s, 1H, ar. H), 8.05 (s, 4H, ar. H), 8.42 (s, 1H, ar. H), 8.57 (s, 1H, ar. H), 9.21 (s, 2H, amide–NH), 9.26 (s, 2H, amide–NH), 9.38 (s, 2H, carbamate NH). – ^{13}C NMR (100.6 MHz, DMSO-d_6, 25 °C): δ/ppm = 18.61, 31.01 (CH_3), 22.82, 25.93, 34.81 (CH_2), 114.16, 114.39, 120.45, 121.05, 125.83, 126.06, 127.57, 127.79, 130.48, 131.32, 131.58 (CH), 34.97, 44.71, 63.74, 64.08, 132.17, 134.58, 134.75, 136.59, 146.20, 146.36, 146.85, 147.44, 148.71, 152.28, 155.28 (C_q), 164.77, 164.97 (C=O).

$C_{122}H_{116}N_6O_8 \cdot CH_3COOC_2H_5$ (1794.3)

Calcd.:	C 80.40	H 6.64	N 4.47
Found:	C 79.91	H 6.52	N 4.56.

[2]{1,3-N,N'-Bis[carboxy(4-(triphenylmethyl)phenoxy)]-xylylene diamine}{11'-(tert-butyl)-5',17',23',35',38',40',43',45'-octamethyldispiro[cyclohexane-1,2'[7,15,25,33]-tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaen-20',1''-cyclohexane]-8',14',26',32'-tetrone}rotaxane (**17**)

722 mg (0.75 mmol) of macrocycle **1** and 141 mg (0.75 mmol) of 1,3-xylylene diisocyanate **11** were dissolved in 100 ml of dichloromethane. This solution was added to a refluxing solution of 571 mg (1.70 mmol) of (4-hydroxyphenyl)triphenylmethane **14** and a few drops of triethylamine in 100 ml of the same solvent over a period of 2 h. The crude product was purified by column chromatography (dichloromethane/ethyl acetate 20:1). *m.p.* > 300 °C, R_f = 0.2 (dichloromethane/ethyl acetate 20:1). Yield 77 mg (6%). MALDI-TOF-MS: *m/z* = 1844.3 $[M + Na]^+$. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm = 1.35 (s, 9H, $C(CH_3)_3$), 1.50 (br, 4H, aliph. CH_2), 1.62 (br, 8H, aliph. CH_2), 1.86 (s, 12H, Ar–CH_3), 1.91 (s, 12H, Ar–CH_3), 2.27 (br, 8H, aliph. CH_2), 3.34 (br, 4H, xylylene–CH_2), 6.90 (s, 4H, ar. H), 6.94 (s, 4H, ar. H), 6.98 (s, 2H, ar. H), 7.00 (s, 2H, ar. H), 7.05 – 7.25 (signal group, 36H, ar. H), 7.51 (br, 1H, ar. H), 7.68 (br, 1H, ar. H), 8.03 (br, 2H, ar. H), 8.15 (s, 2H, ar. H), 8.28 (br, 2H, ar. H), 8.58 (br, 1H, ar. H). – ^{13}C NMR (125.8 MHz, DMSO-d_6, 25 °C): δ/ppm = 18.70, 31.21 (CH_3), 22.34, 26.16, 29.25, 52.21 (CH_2), 120.15, 120.67, 124.39, 125.98, 126.31, 127.91, 130.69, 130.87, 131.55, 131.85 (CH), 35.34, 45.63, 62.76, 132.49, 132.55, 134.47, 134.69, 134.75, 134.83, 142.71, 146.46, 148.98, 154.98 (C_q), 165.09, 165.22 (C=O).

$C_{124}H_{120}N_6O_8 \cdot 2CH_3COOC_2H_5$ (1822.4)

Calcd.:	C 79.33	H 6.86	N 4.21
Found:	C 79.27	H 7.14	N 4.16.

[2]{trans-1,4-N,N'-Bis[carboxy(4-(triphenylmethyl)-phenoxy)]cyclohexylene diamine} {11'-(tert-butyl)-5',17',23',35',38',40',43',45'-octamethyldispiro[cyclohexane-1,2'-[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaen-20',1''-cyclohexane]-8',14',26',32'-tetrone}rotaxane (**18**)

529 mg (0.55 mmol) of macrocycle **1** and 91 mg (0.55 mmol) of *trans*-1,4-cyclohexane diisocyanate **12** were dissolved in 100 ml of dichloromethane. This solution was added to a refluxing solution of 370 mg (1.10 mmol) of (4-hydroxyphenyl)triphenylmethane **14** and a few drops of triethylamine in 100 ml of the same solvent over a period of 2 h. The crude product was purified by column chromatography (dichloromethane/ethyl acetate 20:1). *m.p.* > 300 °C, R_f = 0.3 (dichloromethane/ethyl acetate 20:1). Yield 241 mg (23%). MALDI-TOF-MS: *m/z* = 1823.0 $[M + Na]^+$. – ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ/ppm = 0.33 (br, 8H, aliph. CH_2), 1.30 (s, 9H, $C(CH_3)_3$), 1.45 (br, 4H, aliph. CH_2), 1.54 (br, 8H, aliph. CH_2), 2.02 (s, 12H, Ar–CH_3), 2.03 (s, 12H, Ar–CH_3), 2.29 (br, 8H, aliph. CH_2), 2.62 (br, 2H, aliph. CH), 6.81 (d, ^3J = 8.8 Hz, 4H, ar. H), 6.95 – 7.30 (signal group, 41H, ar. H), 7.60 (t, ^3J = 7.7 Hz, 2H, ar. H), 7.95 (d, ^3J = 7.7 Hz, 2H, ar. H), 7.99 (s, 2H, ar. H), 8.16 (s, 1H, ar. H), 8.31 (s, 1H, ar. H), 9.00 (br, 2H, amide–NH), 9.03 (br, 2H, amide–NH). – ^{13}C NMR (125.8 MHz, DMSO-d_6, 100 °C): d/ppm = 19.11, 19.14, 31.91 (CH_3), 23.66, 26.79, 30.83, 31.80, 35.98 (CH_2), 49.99, 50.07, 115.40, 121.00, 121.02, 126.60, 126.66, 126.83, 126.85, 128.07, 128.17, 128.35, 130.01, 131.27, 131.36, 131.45, 132.17, 132.19, 132.45 (CH), 35.66, 45.86, 133.23, 133.31, 135.49, 135.68, 135.79, 147.43, 147.45, 147.96, 148.36 (C_q), 165.55, 165.77 (C=O).

$C_{122}H_{122}N_6O_8 \cdot 2H_2O$ (1800.4)

Calcd.:	C 79.80	H 6.92	N 4.58
Found:	C 79.50	H 6.91	N 4.50.

[2]{1,6-N,N'-Bis[carboxy(4-(triphenylmethyl)phenoxy)]-hexylene diamine}{11'-(tert-butyl)-5',17',23',35',38',40',43',45'-octamethyldispiro[cyclohexane-1,2'-[7,15,25,33]-tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaen-20',1''-cyclohexane]8',14',26',32'-tetrone}rotaxane (**19**)

529 mg (0.55 mmol) of macrocycle **1** and 93 mg (0.55 mmol) of hexamethylene diisocyanate **13** were dissolved in 100 ml of dichloromethane. This solution was added to a refluxing solution of 370 mg (1.10 mmol) of (4-hydroxyphenyl)triphenylmethane **14** and a few drops of triethylamine in 100 ml of the same solvent over a period of 2h. The crude product was purified by column chromatography (dichloromethane/ethyl acetate 20:1). *m.p.* 278 – 280 °C, R_f = 0.1 (dichloromethane/ethyl acetate 20:1). Yield 144 mg (15%). MALDI-TOF-MS: *m/z* = 1825.2 $[M + Na]^+$. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ/ppm = 0.75 (br, 4H, aliph. CH_2), 1.08 (br, 4H, aliph. CH_2), 1.28 (s, 9H, $C(CH_3)_3$), 1.50 (br, 4H, aliph. CH_2), 1.62 (br, 8H, aliph. CH_2), 1.92 (s, 12H, Ar–CH_3), 1.94 (s, 12H, Ar–CH_3), 2.25 (br, 8H, aliph. CH_2), 2.49 (br, 4H, aliph. CH_2), 6.80 (d, ^3J = 7.8 Hz, 4H, ar. H), 6.87 (s, 8H, ar. H), 7.05 – 7.25 (signal group, 32H, ar. H), 7.41 (t, ^3J = 7.0 Hz, 1H, ar. H), 7.63 (s, 2H, ar. H), 7.71 (s, 2H, ar. H), 7.96

(s, 1H, ar. H), 8.05 (d, ^3J = 7.8 Hz, 1H, ar. H), 8.15 (d, ^3J = 7.0 Hz, 2H, ar. H). – ^{13}C NMR (100.6 MHz, DMSO-d_6, 25 °C): δ/ppm = 18.63, 18.74, 28.57, 30.98 (CH_3), 14.11, 22.73, 25.35, 25.92, 34.76, 44.63 (CH_2), 114.39, 120.38, 125.83, 126.07, 126.18, 127.26, 127.58, 127.70, 130.45, 130.60, 131.22, 131.57 (CH), 35.10, 44.71, 63.97, 132.35, 132.39, 134.19, 134.37, 134.83, 135.02, 142.66, 146.14, 146.25, 146.30, 146.67, 146.86, 148.69, 152.07, 154.27, 154.88 (C_q), 165.44, 165.53, 165.66, 165.78 (C=O).

$C_{122}H_{124}N_6O_8 \cdot H_2O$ (1802.4)

Calcd.:	C 80.50	H 6.98	N 4.62
Found:	C 80.57	H 6.86	N 4.55.

[2]{1,6-N,N'-Bis[carboxy(4-(triphenylmethyl)phenoxy)]-hexylene diamine}{11'-(tert-butyl)-5',17',23',35',38',40',43',45'-octamethyldispiro[cyclohexane-1,2',[7,15,25,33]tetraaza-[26]thiaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaen-20',1''-cyclohexane]-8',14',26',26',32'-pentone}rotaxane (**20**)

499 mg (0.50 mmol) of macrocycle **2** and 84 mg (0.50 mmol) of hexamethylene diisocyanate **13** were dissolved in 100 ml of dichloromethane. This solution was added to a refluxing solution of 336 mg (1.00 mmol) of (4-hydroxyphenyl)triphenylmethane **14** and a few drops of triethylamine in 100 ml of the same solvent over a period of 2 h. The crude product was purified by column chromatography (dichloromethane/ethyl acetate 20:1). *m.p.* 245–247 °C, R_f = 0.4 (dichloromethane/ethyl acetate 20:1). Yield 88 mg (10%). MALDI-TOF-MS: *m/z* = 1 861.2 $[M + Na]^+$. – ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$, 25 °C): δ/ppm = 1.03 (br, 4H, aliph. CH_2), 1.13 (br, 4H, aliph. CH_2), 1.35 (s, 9H, $C(CH_3)_3$), 1.47 (br, 8H, aliph. CH_2), 1.59 (br, 4H, aliph. CH_2), 1.96 (s, 6H, Ar–CH_3), 1.98 (s, 6H, Ar–CH_3), 1.99 (s, 6H, Ar–CH_3), 2.01 (s, 6H, Ar–CH_3), 2.14 (br, 4H, aliph. CH_2), 2.23 (br, 4H, aliph. CH_2), 2.39 (br, 4H, aliph. CH_2), 6.46 (d, ^3J = 8.4 Hz, 4H, ar. H), 6.69 (s, 2H, ar. H), 6.88 (s, 2H, ar. H), 6.94 (s, 8H, ar. H), 7.00–7.20 (signal group, 27H, ar. H), 7.35 (s, 1H, ar. H), 7.55 (t, ^3J = 7.8 Hz, 1H, ar. H), 8.02 (d, ^3J = 7.8 Hz, 1H, ar. H), 8.10 (d, ^3J = 8.4 Hz, 1H, ar. H), 8.20 (s, 2H, ar. H), 8.23 (d, ^3J = 7.0 Hz, 2H, ar. H), 8.28 (s, 1H, ar. H), 8.47 (s, 1H, ar. H). – ^{13}C NMR (100.6 MHz, $CDCl_3/CD_3OD$, 25 °C): δ/ppm = 18.04, 18.47, 18.57, 18.92, 30.73 (CH_3), 22.44, 22.68, 25.93, 26.06, 26.18, 28.89, 34.91, 36.81, 40.57 (CH_2), 119.74, 120.10, 121.80, 125.48, 125.67, 126.04, 126.62, 127.17, 127.31, 128.84, 128.97, 129.31, 129.52, 130.58, 130.69, 130.78, 131.15, 131.64 (CH), 34.98, 44.79, 45.48, 64.13, 132.85, 133.30, 134.61, 134.74, 134.77, 134.85, 137.41, 143.23, 143.57, 144.81, 146.22, 147.23, 148.45, 148.56, 149.92, 153.12, 155.39 (C_q), 164.43, 165.02, 165.35 (C=O).

$C_{121}H_{124}N_6O_9S \cdot H_2O$ (1838.4)

Calcd.:	C 78.29	H 6.84	N 4.53	S 1.73
Found:	C 78.45	H 7.05	N 4.43	S 1.94.

[2]{1,6-N,N'-Bis[carboxy(4-(triphenylmethyl)phenoxy)]hexylene diamine}{11'-(tert-butyl)-5',17',23',35',38',40',43',45'-octamethyldispiro[cyclohexane-1,2'-[7,15,25,33,39]pentaazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaen-20',1''-cyclohexane]-8',14',26',32'-tetrone}rotaxane (**21**)

642 mg (0.67 mmol) of macrocycle **9** and 112 mg (0.67 mmol) of hexamethylene diisocyanate **13** were dissolved in 100 ml of dichloromethane. This solution was added to a refluxing solution of 504 mg (1.50 mmol) of (4-hydroxyphenyl)triphenylmethane **14** and a few drops of triethylamine in 100 ml of the same solvent over a period of 2h. The crude product was purified by column chromatography (dichloromethane/ethyl acetate 10:1). *m.p.* > 300 °C, R_f = 0.5 (dichloromethane/ethyl acetate 10:1). Yield 341 mg (28%). MALDI-TOF-MS: *m/z* = 1 826.1 $[M + Na]^+$. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ/ppm = 1.20 (br, 4H, aliph. CH_2), 1.41 (s, 9H, $C(CH_3)_3$), 1.55 (br, 4H, aliph. CH_2), 1.64 (br, 8H, aliph. CH_2), 1.82 (s, 12H, Ar–CH_3), 1.92 (s, 12H, Ar–CH_3), 2.17 (br, 8H, aliph. CH_2), 2.32 (br, 4H, aliph. CH_2), 3.05 (br, 4H, aliph. CH_2), 6.75 (d, ^3J = 8.1 Hz, 4H, ar. H), 6.86 (s, 8H, ar. H), 6.89 (s, 4H, ar. H), 7.00 – 7.20 (signal group, 28H, ar. H), 7.33 (s, 1H, ar. H), 7.46 (s, 1H, ar. H), 7.77 (s, 1H, ar. H), 8.13 (d, ^3J = 7.5 Hz, 1H, ar. H), 8.22 (s, 1H, ar. H), 8.24 (s, 1H, ar. H), 8.47 (d, ^3J = 7.5 Hz, 2H, ar. H), 8.86 (s, 1H, amide–NH), 8.95 (s, 1H, amide–NH). – ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): d/ppm = 14.21, 18.72, 21.07, 31.29 (CH_3), 22.98, 26.10, 26.34, 29.50, 35.98, 41.13 (CH_2), 120.07, 125.47, 126.04, 126.16, 126.60, 126.78, 126.92, 127.55, 129.01, 130.35, 130.84, 130.97, 131.05, 131.22, 131.68, 131.90 (CH), 35.40, 45.20, 64.34, 134.30, 134.36, 134.79, 134.95, 143.73, 146.47, 148.24, 148.65, 149.05, 153.92, 155.22 (C_q), 161.09, 161.20, 165.21, 165.36, 171.20 (C=O).

$C_{121}H_{123}N_7O_8 \cdot 2CH_3COOC_2H_5$ (1803.4)

Calcd.:	C 78.27	H 7.08	N 4.95
Found:	C 78.63	H 7.03	N 5.08.

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