Rotaxanes with Chiral Stoppers and Photoresponsive Central Unit

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Abstract: Two new chiral and photoisomerizable rotaxanes (**9m, 9p**) have been prepared, bearing the longest non-polymeric axle known so far: the axles (**6m**, **6p**) are polyether chains made of alternating triethyleneglycol/hydroquinone units, bearing a central *meta*- or *para*-azobenzoyl moiety and terminal tetraacetylglucoside stopper groups, while the wheel is the cyclobis(*p*-xylylene)bis(4,4´-bipyridinium) salt. Temperature dependent ^{1}H NMR measurements reveal that the translational process of the wheel across the azobenzene unit in the *E*-configuration is favoured for the para-rotaxane **9p** compared to the meta isomer **9m**. The azobenzene core of the free axles (**6m**, **6p**) and rotaxanes (**9m, 9p**) undergo photochemical *E*/*Z*-isomerisation: from (*E*) to (*Z*) by irradiation at low wavelength and back from (*Z*) to (*E*) at high wavelength. Complete (*Z*) to (*E*) conversion was achieved by thermal isomerization.

Key words: rotaxane, azobenzene isomerization, molecular recognition, chirality, supramolecular chemistry

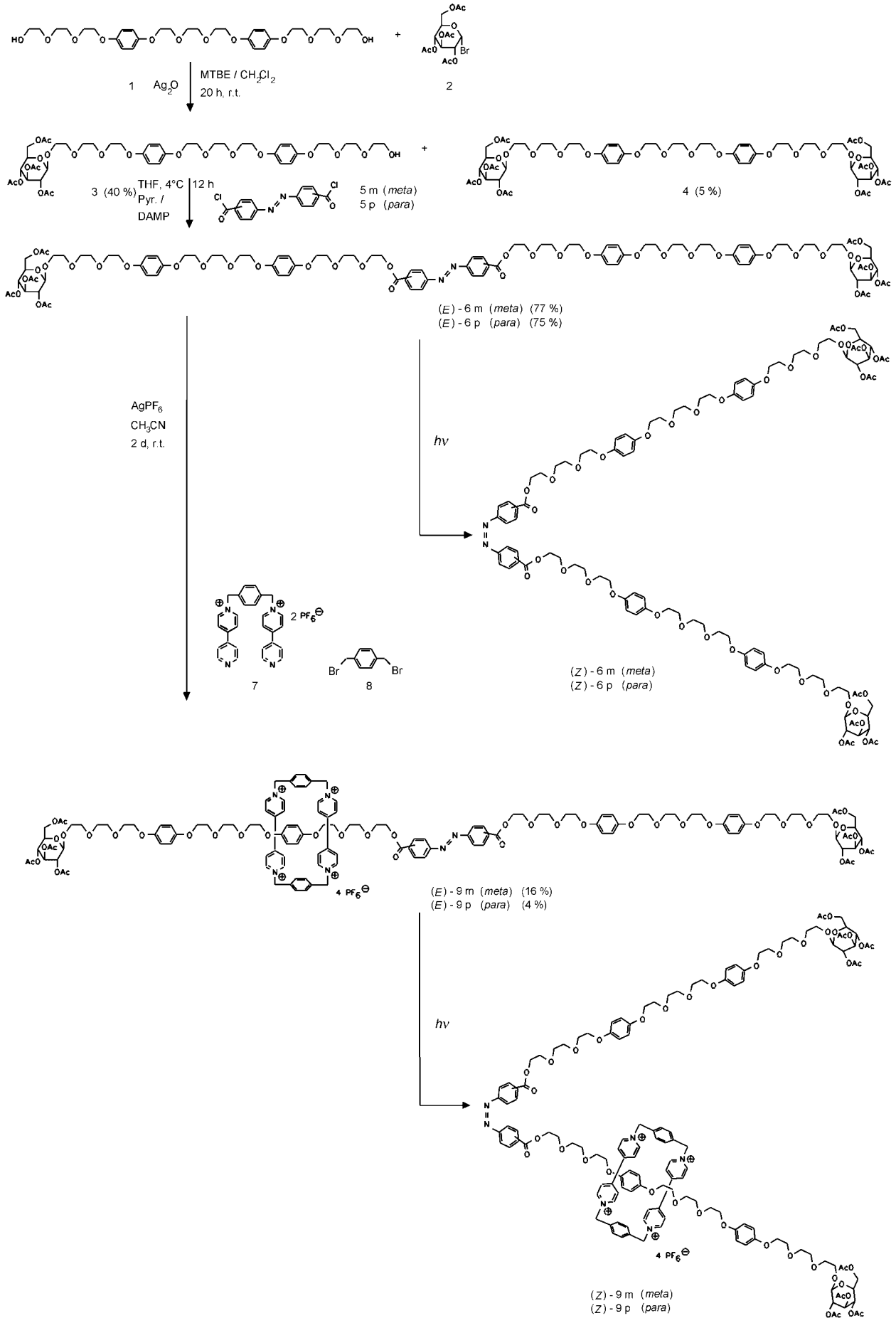
Azobenzene derivatives have been used to construct photoswitchable devices for many years.[1–3] The thermodynamically stable (*E*)-isomer can usually be photochemically converted to the (*Z*)-isomer,[4] which is converted back to the (*E*)-isomer by light excitation and thermally in the dark.[5]

For the synthesis of the title rotaxanes **9**,[6] we started with the hydroquinone derived ethyleneglycol **1**[7] and α-D-acetobromoglucose **2**[8] to yield the chiral mono-stoppered half-axle **3** and, as a byproduct, the doubly tetraacetylglucoside stoppered short chain **4**.[7] By use of $HgBr_2$/$Hg(CN)_2$ in MeCN instead of Ag_2O in CH_2Cl_2/*t*-BuOMe in this reaction step, formation of the chiral di-stoppered axle **4** is favoured, as we recently reported.[7] By reaction of the tetraacetyl-β-D-glucoside stoppered glycol **3** with the *meta*- or *para*-azobenzoic acid dichlorides (**5m, 5p**), the chiral axles **6m** and **6p** were obtained, respectively, in 75% yield. The cyclobis(*p*-xylylene)bis(4,4´-bipyridinium) wheel of the rotaxanes was cyclized using the clipping method worked out by Stoddart et al.,[4b,c] by reaction of the 1,1´-*p*-xylylenebis(4,4´-bipyridinium) bis(hexafluorophosphate) salt **7** with 1,4-bis(bromomethyl)benzene (**8**) in presence of the axles **6p** or **6m**, to yield the chiral *meta*- or the *para*-rotaxanes **9p** or **9m**, respectively. They were isolated mainly in the (*E*)-configuration, but depending on light exposure, they may contain small amounts of the (*Z*)-form.

The axles **6m**, **6p** and the rotaxanes **9m**, **9p** were characterized by FAB and MALDI mass spectrometry, by NMR and CD spectroscopy.[9] The isolated main fraction of the sugar-stoppered axles clearly exhibits β-glucosidic connections as could be confirmed by ^{1}H NMR measurements. This implication can directly be derived from the value of the H-1/H-2 coupling constants of the terminal sugar groups ($^3J_{H\text{-}1,H\text{-}2}$ = 7.9 and 8.0 Hz), which are in good agreement with axially positioned hydrogen atoms at the C-1 and C-2 positions within a glucose unit.[10] Smaller coupling constants, which would be exhibited by an α-glucosidic connection (H-1 in an equatorial, H-2 in axial position) could not be detected.

The rotaxanes described present a world record regarding the length of a non-polymeric axle moiety. We chose these long axles to examine if the translational movement of the wheel along the axle can be systematically influenced compared to similar rotaxanes with a shorter axle[7,11], which could be detected by NMR measurements. At ambient temperature the electron-deficient wheel component, which prefers the proximity of the electron-rich hydroquinone system, is in a translational movement mainly along one side of the azobenzene unit, that is, without slipping over. Since this movement is already slow enough at r.t. on the NMR time scale, the signals for the hydroquinone protons of the "unoccupied side" show up at δ = 6.7–6.9 ppm, whereas the signals for the hydroquinone protons of the "occupied" side are merged in the base line at higher magnetic field as already described accurately in the literature for similar rotaxanes.[7,11]

In DMSO-d_6 at 45 °C, the former broaden significantly to likewise merge in the baseline for both rotaxanes. At 65 °C, in the case of the para-rotaxane **9p,** a distinct coalescence signal at δ = 6.15 ppm can be detected, while for the meta-rotaxane **9m**, the corresponding signals are still extremely broadened. At 85 °C, however, no difference between the shape of the coalescence signals of both compounds can be observed anymore. Thus, our NMR studies indicate that the shuttle process of the tetracationic cyclophane across the azobenzene unit is slightly disfavoured for the meta-rotaxane compared to the para-substituted compound. Low temperature ^{1}H NMR studies down to –60 °C in acetone-d_6 lead to a complicated signal splitting for both the wheel and the axle, so that a coalescence temperature for the translational process of the cyclophane between two neighbouring hydroquinone units cannot be determined.



In attempts to prepare rotaxanes bearing the isomeric wheel of cyclo(*p*-xylylene/*m*-xylylene)bis-4,4´-bipyridinium salt under analogous conditions, both the free wheel and the free axle components were isolated but no rotaxane could be detected. This may be due to the smaller wheel perimeter as well as to an unfavourable torsional disposition of the aromatic rings.

The (*E*)-*meta*-axle ((*E*)-**6m**) underwent (*E*) → (*Z*) photoisomerization on irradiation at 338 nm. This is manifested by a shift to lower wavelength and an increase in intensity of the > 400 nm absorption maximum.

Quantum yield was measured (on concentrated solutions) and found to be $\phi = 0.1$. The photostationary state exhibited a ca. 95% (*Z*)-**6m** content (measured by both, UV and NMR methods). Four isosbestic points at 232, 257, 269 and 375 nm indicate "pure" (*E*) → (*Z*) isomerization.

Irradiation of the (*Z*)-axle (*Z*)-**6m** in the above (*Z*)-enriched product at 446 nm gave a (*E*)/(*Z*) mixture of 3/1 (by NMR), and $\phi_E/\phi_Z = 2.3$ at 446 nm. Finally, the thermal (*Z*)-**6m** → (*E*)-**6m** isomerization was measured by NMR spectroscopy in toluene-d_8 with a half-life time of 60 min at 95°C and 270 min at 60°C.

The *meta*-rotaxane (*E*)-**9m** was irradiated at 338 nm for photoisomerization to the (*Z*)-form. Three isobestic points were observed at 256, 270, 378 nm. The quantum yield is similar as for *(E)*-**6m**, $\phi = 0.06$.

The thermal (*Z*)-**9m** → (*E*)-**9m** process takes place at room temperature with a half-life time of ca. 200 h.

The (*E*)-*para*-axle (*E*)-**6p** was irradiated in the 311–365 nm range, which caused (*E*) → (*Z*) photoisomerization. At the most effective 345±6 nm irradiation, a photostationary state with a ca. 72% (*Z*)-**6p**-content was reached. The quantum yield in this process was determined to give $\phi = 0.02$ with a 20% uncertainty margin. The photoisomerization is again indicated by the occurrence of four isobestic points at 240, 283, 383 and 490 nm.[12]

The (*Z*)-*para*-axle (*Z*)-**6p** in the above (*Z*)-enriched photochemical product was irradiated at 446 nm, which caused nearly total reversal to (*E*)-**6p** (the relative quantum yield at this wavelength could be estimated: $\phi_{Z\rightarrow E}/\phi_{E\rightarrow Z} \geq 10$). Complete (*Z*) → (*E*) reversal could, however, be achieved by heating the sample. Indeed, this thermal (*Z*) → (*E*) isomerization was readily measured (by NMR at the $\delta = 7.6$ ppm signals) and exhibits, at 60 °C, a first-order rate constant of $k_1 = 1.3 * 10^{-4}$ sec^{-1}, i.e., a half-life time of 88 min. This is in accord with the behaviour of simply substituted azobenzenes.[13]

According to space filling models, the *(E)* → (*Z)* isomerization generates a stopper-like barrier for the wheel, thus the isomerization process was supposed to be associated with a reduced translational distance for the wheel along the axle. Hence, the mechanical frequency of this translational movement should about double at a given temperature, since the effective length for this motion was cut in half. This "mechanical frequency doubling" in going from the *(E)* to the *(Z)*-isomer, a switching of conformational mobility, respectively, one of the original aims of this study, yet could not be determined unequivocally, as prolonged irradiation seems to lead to byproducts that additionally complicate the interpretation of UV, as well as NMR spectra compared to our earlier investigations.[2,14]

Mps: Tottoli-type melting point apparatus SMP-20 (Büchi), and are uncorrected. TLC: TLC plastic sheets with silica gel (SiO_2) 60 F_{254} (Merck 5748). Detections: UV or development with iodine vapor. Column chromatography: preparative medium pressure chromatography system (MPLC) by Büchi. CHN analyses: Mikroanalytisches Labor Pascher, Remagen, Germany. Optical rotations were recorded at r.t. with a Perkin-Elmer model 241 automatic polarimeter. ^{1}H and ^{13}C NMR: Bruker AC-200 Cryospec (200 MHz and 50.3 MHz), AC-360-WB (360 MHz and 90.5 MHz), WM 250 (250 MHz and 62.9 MHz), AM 400 (400 MHz and 100.6 MHz) and DRX 500 (500 MHz, for the temperature dependent measurements) spectrometers. MS: MS-30 and MS-50 A.E.I. instruments. FAB-MS spectra were obtained on a Concept 1H, Cratos, Manchester, UK in NBA (*m*-nitrobenzyl alcohol) as matrix. MALDI-TOF spectra were recorded with a Micromass TOF Spec E (Micromass, Manchester, UK); the matrices used were 9-nitroanthracene (9-NA) and 2,5-dihydroxybenzoic acid (2.5-DHB). UV spectra were measured on a UVIKON-931 spectrophotometer.

Photochemical experiments were performed on a JASCO CRM-FA Spectro-irradiator, equipped with a photon-counter. For quantum yields, the latter was periodically calibrated by chemical actinometry (using the Aberchrome 540 actinometer); at 338 nm the output was $2.5*10^{-8}$ Einstein/s. The usual bandwidth for 1 cm cells was ±13 nm; when needed, this range was reduced by using narrower windows. Irradiations were carried out, for both preparative and analytical purposes, at 338 nm. All irradiations were performed on deoxygenated (Ar or N_2) MeCN solutions in quartz (< 300 nm) or pyrex (300–500 nm) UV cells or NMR tubes. The products of the preparative runs at 338 nm were used for thermokinetic studies in NMR tubes held at constant temperatures, kept by reflux of various solvents (e.g., $CHCl_3$ for 60 °C). Both photochemical and thermochemical experiments were monitored using UV and/or ^{1}H NMR spectroscopy.

β-D-Glucoside 3

Compound **1**[7] (17.95 g, 30 mmol) was dissolved in anhyd CH_2Cl_2 (100 mL) and diluted with anhyd *t*-BuOMe (200 mL), and 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide **2**[8a,b] (13.57 g, 33 mmol) was added. After the reaction flask had been wrapped by aluminium foil freshly precipitated Ag_2O (6.95 g, 30 mmol) was added to the mixture. It was stirred overnight at r.t. The progress of the reaction was monitored by TLC. The solution was filtered through Celite. The solvent was evaporated. The remaining residue was dissolved in CH_2Cl_2 and separated by MPLC using Lichroprep Si 60 (15–25 μm) with CH_2Cl_2/MeOH (9.8:0.2) as eluent. Yield: 11.2 g (40%).

After recrystallization from THF, mp 59–60 °C. $[\alpha]_D^{21} = -2.7$ (*c* = 0.9, in $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.97–2.08 (m, 12H, $OCCH_3$), 2.56 (br s, 1H, OH), 3.57–4.14 (m, 36H, OCH_2), 4.20–4.27 (m, 1H, 5-H), 4.59 (d, 1H, $^3J_{H,H}$ = 8.1 Hz, 1-H), 4.97 (dd, 1H, $^3J_{H,H}$ = 8.1 Hz, $^3J_{H,H}$ = 9.6 Hz, 2-H), 5.06 (t, 1H, $^3J_{H,H}$ = 9.5 Hz, 4-H), 5.18 (t, 1H, $^3J_{H,H}$ = 9.5 Hz, 3-H), 6.82 (s, 8H, ar. H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 20.61, 20.65, 20.69, 20.77 ($OCCH_3$), 61.76, 61.93, 67.99, 68.03, 69.13, 69.85, 69.89, 70.34, 70.35, 70.74, 70.78, 70.79, 70.83, 71.26, 71.75, 72.52, 72.83 (CH_2, glucose-CH), 100.85, 115.51, 115.57, 115.59 (ar. CH),

152.98, 153.04, 153.10, 153.15 (C_q), 169.45, 169.46, 170.32, 170.74 (C=O).

$C_{44}H_{64}O_{21}$: calc. C 56.8, H 6.94; found C 57.1, H 7.25.

FAB-MS: *m/z* = 928.4 (M^+).

As a byproduct, the β-D-bisglucoside **4**[7] was isolated. Yield: 2.2 g (5%).

$[\alpha]_D^{21}$ = 5.29 (*c* = 1.6, in $CHCl_3$).

FAB-MS: *m/z* = 1258.5 (M^+).

***meta*-Axle 6m**

At r.t. **3** (7.83 g, 8.43 mmol) and *m*-azobenzoic acid dichloride **5m** (1.29 g, 4.2 mmol) were dissolved in THF (40 mL). After the solution had been cooled to +4°C, a solution of pyridine (0.67 g, 8.48 mmol) and a few crystals of 4-dimethylaminopyridine in THF (10 mL) were added dropwise under stirring. After 12 h the precipitate was filtered off and the solvent was evaporated. The residue was separated using Lichroprep Si 60 (15–25 μm) with CH_2Cl_2/MeOH (9.75:0.25) as eluent, to give **6m** as a reddish oil. Yield: 6.78 g (77%). $[\alpha]_D^{21}$ = -16.5 (*c* = 1.8, in $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.95–2.15 (m, 24H, $OCCH_3$), 3.58–4.15 (m, 72H, OCH_2), 4.19–4.29 (m, 2H, 5-H), 4.48–4.56 (m, 4H, CH_2OAc), 4.59 (d, 2H, $^3J_{H,H}$ = 8.0 Hz, 1-H), 4.98 (dd, 2H, $^3J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 9.6 Hz, 2-H), 5.06 (t, 2H, $^3J_{H,H}$ = 9.6 Hz, 4-H), 5.19 (t, 2H, $^3J_{H,H}$ = 9.5 Hz, 3-H), 6.79 (s, 8H, ar. H), 6.82 (s, 8H, ar. H), 7.58 (t, 2H, $^3J_{H,H}$ = 7.9 Hz, ar. H), 8.10 (dt, 2H, $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,H}$ = 1.2 Hz, ar. H), 8.17 (dt, 2H, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.5 Hz, ar. H), 8.60 (t, 2H, $^4J_{H,H}$ = 1.7 Hz, ar. H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 20.62, 20.66, 20.69, 20.78 (OC*C*H_3), 61.91, 64.45, 67.96, 69.14, 69.19, 69.88, 70.34, 70.73, 70.75, 70.81 (CH_2), 68.35,, 71.23, 71.73, 72.81 (glucose-CH), 100.84, 115.47, 115.53, 124.57, 126.87, 129.31, 132.24 (ar. CH), 131.35, 152.31, 153.02 (C_q), 153.04. 153.07, 165.90, 169.42, 169.45, 170.30, 170.71 (C=O).

FAB-MS: *m/z* = 2091.6 (M^+).

***para*-Axle 6p**

At r.t. **3** (6.35 g, 6.84 mmol) and *p*-azobenzoic acid dichloride **5p** (1.05 g, 3.42 mmol) were dissolved in THF (40 mL). After the solution had been cooled to +4°C, a solution of pyridine (0.54 g, 6.84 mmol) and a few crystals of 4-dimethylaminopyridine in THF (10 mL) were added dropwise under stirring. After 24 h the precipitate was filtered off, and the solvent was evaporated. The residue was separated using Lichroprep Si 60 (15–25 μm) with CH_2Cl_2/MeOH (9.75:0.25) as eluent, to give **6p** as a reddish oil. Yield: 5.4 g (75%). $[\alpha]_D^{21}$ = -6.3 (*c* = 1.4, in $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.85–2.10 (m, 24H, $OCCH_3$), 3.50–4.06 (m, 72H, OCH_2), 4.15–4.25 (m, 2H, 5-H), 4.41–4.51 (m, 4H, CH_2OAc), 4.55 (d, 2H, $^3J_{H,H}$ = 7.9 Hz, 1-H), 4.92 (dd, 2H, $^3J_{H,H}$ = 8.0 Hz, $^3J_{H,H}$ = 9.5 Hz, 2-H), 5.01 (t, 2H, $^3J_{H,H}$ = 9.4 Hz, 4-H), 5.15 (t, 2H, $^3J_{H,H}$ = 9.4 Hz, 3-H), 6.78 (s, 8H, ar. H), 6.80 (s, 8H, ar. H), 7.90 (d, 4H, $^3J_{H,H}$ = 8.5 Hz, ar. H), 8.15 (d, 4H, $^3J_{H,H}$ = 8.5 Hz, ar. H).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 20.53, 20.60, 20.66 (OC*C*H_3), 61.85, 64.39, 67.93, 69.03, 69.09, 69.78, 70.25, 70.71 (CH_2), 68.31, 71.19, 71.66, 72.75 (glucose-CH), 100.74, 115.47, 115.48, 115.50, 115.52, 122.87, 130.70 (ar. CH), 132.32, 152.96, 153.01 (C_q), 154.80, 165.73, 169.34, 170.14 (C=O).

FAB-MS: *m/z* = 2091.7 (M^+).

***meta*-Rotaxane 9m**

Under Ar **6m** (5.32 g, 2.54 mmol) and 4-pyridin-4-yl-1-({4-[(4-pyridin-4-ylpyridinium-1-yl)methyl]phenyl}methyl)pyridinium dihexafluorophosphate (**7**) (0.901 g, 1.275 mmol) were dissolved in anhyd MeCN (160 mL). After 15 min 1,4-bis(bromomethyl)benzene (**8**) (0.35 g, 1.325 mmol) and silver hexafluorophosphate (0.74 g, 2.88 mmol) were added. The mixture was stirred for 2d under the exclusion of light. After filtration the solvent was evaporated. The residue was dissolved in nitromethane (60 mL), and a solution of Et_4NCl in nitromethane (8 mL, 20%) was added. The water-soluble precipitate was separated by MPLC using Lichroprep Si 60 (15–25 μm) with MeOH/1 M NH_4Cl/ nitromethane (7:2:1). Yield: 640 mg (16%). $[\alpha]_D^{21}$ = -1.7 (*c* = 1.55, in acetone).

^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ = 1.83–2.15 (m, 24H, $OCCH_3$), 3.57–4.15 (m, 72H, OCH_2), 4.19–4.29 (m, 2H, 5-H), 4.53 (br s, 4H, CH_2OAc), 4.77 (br s, 2H, 1-H), 4.90 (dd, 2H, $^3J_{H,H}$ = 7.9 Hz, $^3J_{H,H}$ = 9.6 Hz, 2-H), 5.01 (t, 2H, $^3J_{H,H}$ = 9.6 Hz, 4-H), 5.21 (br s, 2H, 3-H), 5.99 (s, 8H, NCH_2), 6.79 (s, 4H, ar. H), 6.85 (s, 4H, ar. H), 7.76 (t, 2H, $^3J_{H,H}$ = 7.5 Hz, ar. H), 7.98–8.59 (m, 22H, ar. H), 9.33 (br s, 8H, bipy-H).

^{13}C NMR (100.6 MHz, acetone-d_6, 25 °C): δ = 20.59, 20.65, 20.72 (OC*C*H_3), 55.45, 62.81, 65.39, 65.78, 68.81, 69.67, 69.89, 70.47, 70.86, 71.09, 71.31, 71.41, 71.82 (CH_2), 69.44, 72.16, 72.37, 73.50 (glucose-CH), 101.42, 116.25, 116.30, 123.88, 126.90, 130.92, 131.61, 145.89 (ar. CH), 124.31, 132.61, 133.09, 137.80, 147.65 (C_q), 153.09, 154.09, 166.20, 169.90, 170.13, 170.85 (C=O).

MALDI -TOF (2,5-DHB): *m/z* = 2757.2 (M^+ - 4 PF_6; + Na^+).

$C_{138}H_{164}N_6O_{44}P_4F_{24}\cdot 3\,H_2O$ (3244.73): calc. C 51.08, H 5.28; found C 50.74, H 5.29.

After the evaporation of the nitromethane mother liquor, the unreacted axle **6m** was recovered by $CHCl_3$ extraction.

***para*-Rotaxane 9p**

As described for **9m** the rotaxane **9p** is formed from **6p** (3.66 g, 1.75 mmol), **7** (0.62 g, 0.875 mmol), **8** (0.24 g, 0.9 mmol), silver hexafluorophosphate (0.51 g, 2 mmol) in MeCN (130 mL). Yield: 120 mg (4%). $[\alpha]_D^{21}$ = -4.1 (*c* = 1.25, in acetone).

^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ = 1.80–2.15 (m, 24H, $OCCH_3$), 3.55–4.15 (m, 72H, OCH_2), 4.18–4.30 (m, 2H, 5-H), 4.52 (br s, 4H, CH_2OAc), 4.77 (br s, 2H, 1-H), 4.90 (dd, 2H, $^3J_{H,H}$ = 8.1 Hz, $^3J_{H,H}$ = 9.8 Hz, 2-H), 5.02 (t, 2H, $^3J_{H,H}$ = 9.4 Hz, 4-H), 5.20 (br s, 2H, 3-H), 6.00 (s, 8H, NCH_2), 6.83 (s, 4H, ar. H), 6.86 (s, 4H, ar. H), 7.95–8.35 (m, 24H, ar. H), 9.36 (d, 8H, $^3J_{H,H}$ = 5.8 Hz, bipy-H).

^{13}C NMR (100.6 MHz, acetone-d_6, 25°C): δ = 20.58, 20.64, 20.71 (OC*C*H_3), 55.47, 62.80, 65.39, 65.79, 68.81, 69.88, 70.48, 70.87, 71.08, 71.41 (CH_2), 69.44, 72.16, 72.37, 73.50 (glucose-CH), 101.41, 116.29, 116.31, 123.87, 126.92, 130.89, 131.61, 145.91 (ar. CH), 128.11, 137.82, 147.68 (C_q), 154.10, 166.15, 170.13 (C=O). $C_{138}H_{164}N_6O_{44}P_4F_{24}\cdot 4H_2O$ (3262.75): calc. C 50.80, H 5.31; found C 50.94, H 5.31.

MALDI-TOF (2,5-DHB): *m/z* = 2756.9 (M^+ -4 PF_6; + Na^+).

After the evaporation of the nitromethane mother liquor, the unreacted axle **6p** was recovered by $CHCl_3$ extraction.

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