EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201402249

A Shuttle for the Transport of Protons Based on a [2]Rotaxane

Britta Hesseler,[a] Melanie Zindler,[a] Rainer Herges,[a] and Ulrich Lüning*[a]

Keywords: Supramolecular chemistry / Rotaxanes / Macrocycles / Click chemistry / Hydrogen bonds

A [2]rotaxane shuttle for (light-driven) proton transport has been designed and synthesized. The rotaxane contains a macrocyclic ring that carries a pyridine nitrogen atom as a basic center to bind and to transport a proton. The axis includes an amide binding site for the macrocycle and a positive charge in close vicinity. Upon protonation of the pyridine nitrogen atom, the hydrogen bond is broken and Coulomb repulsion between the protonated pyridine and the permanent positive charge in the axis pushes the protonated macrocycle to the other end of the axis. By variation of the pH the ring can shuttle to and fro. Its locations on the axis were determined by NMR spectroscopy.

Introduction

Mechanical motion not only plays a crucial role in the macroscopic world, it is also essential for a number of natural and artificial molecular processes.[1–3] One of the prototypes of molecular machines in nature is ATPase[4] that produces about 35 kg ATP per capita per day. The energy source is a pH gradient,[4] which is generated by photosynthesis (in green plants) or by metabolism of glucose. In halobacteria, the pH gradient is built up across a biological membrane by bacteriorhodopsin, a light-driven proton pump.[5]

A rotaxane-based artificial light-driven proton pump,[6,7] must include the following features: at one side of the membrane light must generate a low pH, and to pick up the protons and to transport them to the other side of the membrane, a transport mechanism is needed. The general design of our rotaxane shuttle aimed at performing such transport is shown in Figure 1. Rotaxanes are mechanically interlocked molecules in which a ring is able to move along an axis. Two stoppers on either end of the rotaxane prevent the ring from slipping off the axis. Since the first synthesis of a rotaxane,[8,9] numerous interlocked molecules have been synthesized.[10] For the purpose of a light-driven proton pump a rotaxane with a resting station next to one stopper has to be synthesized. The ring of the rotaxane must be able to pick up a proton on one side, and then it must move to the other side, release the proton, and diffuse back.

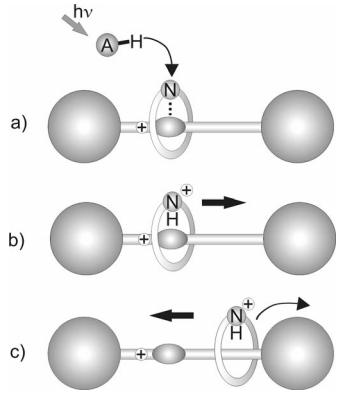


Figure 1. Schematic representation of a light-driven proton pump. (a) A mixture of a [2]rotaxane and a photo acid A-H is irradiated by light. The [2]rotaxane contains a ring with a basic nitrogen atom and an axis in which a binding site for the ring exists next to a permanent positive charge. Upon irradiation, the acidity of A-H is increased and the photo-acid can protonate the basic nitrogen atom in the ring of the rotaxane. (b) The resulting positively charged macrocyclic ring is repelled by a permanent positive charge in the axis of the rotaxane. (c) When the ring eventually releases the proton, the resulting neutral macrocycle can diffuse back to the starting point.

Over the years, [2]rotaxanes with axes containing various binding sites have been investigated as molecular shuttles.[11] For a shuttle as shown in Figure 1, a ring including a basic center must be able to move along an axis which has a binding site on one side for the unprotonated ring. After protonation however, the protonated ring is repelled so that it moves to the other side of the rotaxane. For this purpose the axis needs to contain a positive charge close to the binding site.

An amide unit was chosen as the binding site for the basic macrocycle. The macrocyclic ring contains a 2,6-disubstituted pyridine. The 2,6-disubstitution orients the pyr-

[a] Otto-Diels-Institut für Organische Chemie,
Christian-Albrechts-Universität zu Kiel,
Olshausenstraße 40, 24098 Kiel, Germany
E-mail: luening@oc.uni-kiel.de
http://www.luening.otto-diels-institut.de/

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201402249.

idine nitrogen atom to the inside of the macrocycle to allow docking to the amide NH. By protonation, the hydrogen-bond acceptor, the pyridine nitrogen atom, becomes a hydrogen-bond donor. This would allow a hydrogen bond to form with the carbonyl group of the amide. However, the positive charge generated by protonation of the pyridine in the ring and the permanent positive charge on the axis repel each other and push the ring towards the other end of the axis.

Thus, the desired [2]rotaxane must consist of a pyridine macrocycle and a positively charged axis. Examples of both components of the rotaxane are described in the literature. 2,6-Disubstituted pyridine macrocycles can be synthesized in a variety of ways.[12] We have chosen a 4-substituted 2,6-bis(bromomethyl)pyridine as starting material, substituted the bromine atoms by alkenyl-substituted ethers, and then used ring-closing metathesis for the macrocycle formation.[13] Axes with positive charges, such as protonated amines, have often been used in rotaxane syntheses and there are also examples of rotaxanes with permanent positive charges in the axis.[14–18].

Finally, a suitable synthetic method must be chosen for assembly of the rotaxane. Most rotaxane syntheses exploit strong supramolecular interaction between the components to generate the rotaxane in good yield, for instance by threading or clipping.[10] But in the case of the light-driven proton pump, preferentially no additional functional groups should be introduced because they might interfere with the shuttling process. The macrocyclic ring contains only one functional group, which can be incorporated in an assembly process, the pyridine heterocycle. Macrocycles that contain N-heterocycles have been used in trapping syntheses of rotaxanes.[19–21] In such a trapping process, the axis is formed from two half axes, which are connected inside the macrocycle. As nitrogen atoms bind well to transition metal ions, metal-ion-catalyzed reactions can be performed in the trapping mode, for instance copper(I)-catalyzed 1,3-dipolar cycloaddition reactions (click chemistry).[19]

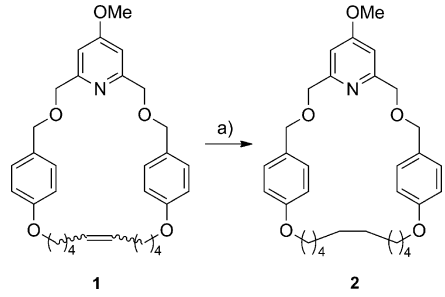
To realize the proton shuttle depicted in Figure 1, we therefore needed: a pyridine containing macrocycle; one half axis terminated by an alkyne; and one half axis terminated by an azide. As stoppers, tris(*tert*-butylphenyl)methyl groups were chosen because they had proven to be large enough for use with a 29-membered ring containing a pyridine ring.[19]

In contrast to other rotaxanes which can be switched by pH changes,[11] the protonatable/deprotonatable function in our system is located on the ring and the repelling positive charge is part of the axis.[22] Thus the protonation/deprotonation process is coupled with movement of the protons along the axis as needed for a proton pump. Movement of a macrocycle upon protonation has been observed with related pseudorotaxanes,[23,24] but of course, these pseudorotaxanes disassemble upon protonation. In this work, we present the synthesis of a rotaxane that contains the mobile protonatable site in the ring. The movement and its reversibility have been investigated by pH titrations.

Results and Discussion

Synthesis of the Macrocycle

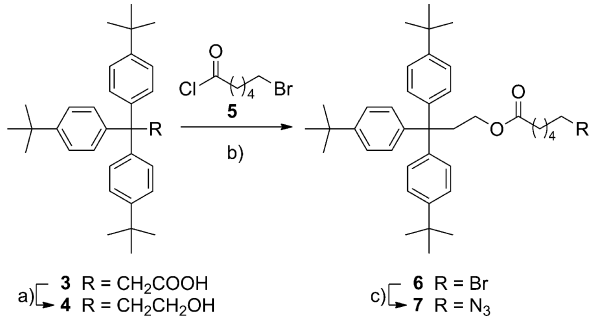
The synthesis of 29-membered pyridine macrocycles was already known.[13] Although saturated ring **2** was obtained by a double Williamson-ether synthesis, its unsaturated relative **1** was synthesized by a ring-closing metathesis in considerably better yields. In principle, this macrocycle could serve as the proton carrier but it is generated as a mixture of *E* and *Z*. Therefore, **1** was hydrogenated with platinum oxide as the catalyst to give saturated macrocycle **2** in 99% yield (Scheme 1).



Scheme 1. Synthesis of the macrocycle **2**. (a) H_2, PtO_2, $CHCl_3$, 2 d, room temp., 99%.

Synthesis of the Azide Half-axis

Azide half-axis **7** was prepared in three steps starting from known tris(*tert*-butylphenyl)methyl stopper derivative[25] **3** (Scheme 2). With thionyl chloride, propanoic acid derivative **3** was converted into the respective acid chloride that was then directly reduced with lithium aluminum hydride to yield propanol derivative **4** in 71% yield. Alcohol **4** was then treated with 6-bromohexanoic acid chloride[26] (**5**) to give ester **6** in 81% yield. Finally, bromide **6** was converted into azide **7** in 89% yield by nucleophilic substitution with sodium azide.

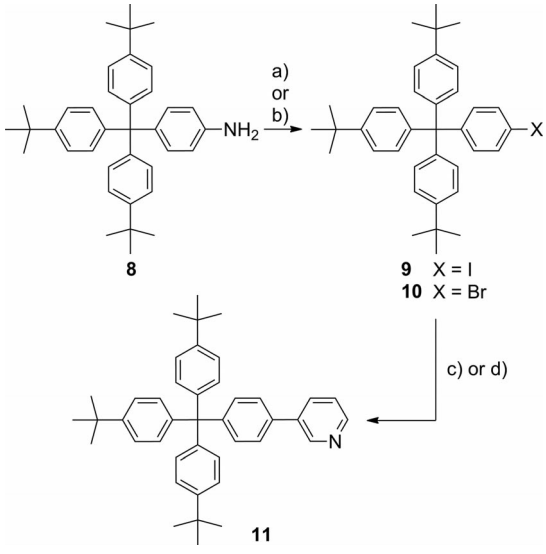


Scheme 2. Synthesis of azide half-axis **7**. (a) (i). $SOCl_2$, 2.5 h, reflux, (ii). LAH, diethyl ether, 2 h, reflux, 71%; (b) Et_3N, CH_2Cl_2, 19 h, reflux, 81%; (c) NaN_3, DMF, 2 d, 80 °C, 89%.

Synthesis of the Alkyne Half-Axis

The second half of the rotaxane axis, alkyne half-axis **22**, was synthesized in a convergent way from pyridine **11**

(Scheme 3) and alkyne linker **20** (Scheme 4). By converting aniline[27] **8** into the respective diazonium salt, iodinated and brominated stoppers **9** and **10** were synthesized in 68% and 52% yield, respectively. Through palladium-catalyzed cross-coupling reactions halogenated stoppers **9** and **10** were then coupled to a pyridine. In the case of iodide **9**, a Stille coupling reaction with 3-(tributyltin)pyridine was performed to give pyridine **11** in 38% yield. Alternatively, bromide **10** was coupled in a Suzuki–Miyaura reaction with 2-(3-pyridyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[28] to yield pyridine **11** in 26%. Iodide **9** was also employed in the Suzuki–Miyaura coupling and bromide **10** in the Stille coupling. Both reactions worked as well, but gave pyridine **11** in lower yields.



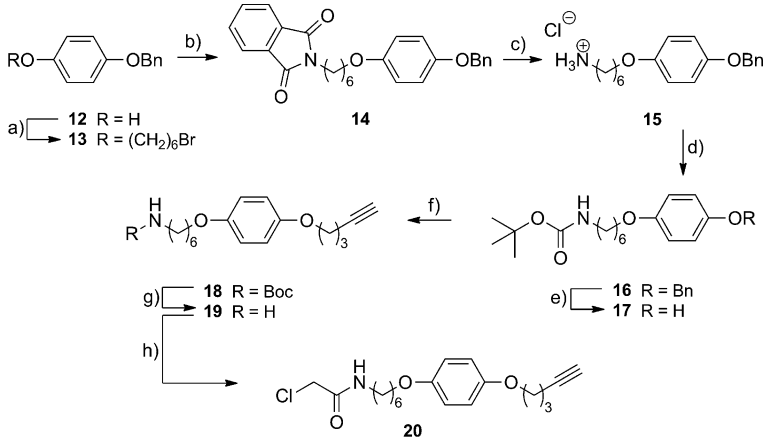
Scheme 3. Synthesis of pyridine half-axis **11**. (a) (i). $NaNO_2$, acetone, HCl, 30 min, 0 °C, (ii). KI, 1 h, room temp., then 2 h at 60 °C, 68%; (b) (i). $NaNO_2$, acetone, HBr solution, 1 h, 0 °C, (ii). CuBr, 3 h, room temp., 52%; (c) 2-(3-pyridyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, $Ba(OH)_2{\cdot}8H_2O$, $Pd(OAc)_2$, dppp, DME/H_2O (4:1), 1 d, reflux, 26% (X = I); (d) 3-(tributyltin)pyridine, $(Ph_3P)_2Pd^{II}Cl_2$, CuI, DMF, 1 d, 100 °C, 38% (X = Br).

For the synthesis of alkyne linker **20**, monobenzyl-protected hydroquinone **12** was treated with potassium carbonate and 1,6-dibromohexane to yield alkylated ether **13** in 69%. The remaining bromine atom in **13** was substituted by phthalimide to yield **14** in 95% yield (Gabriel synthesis). Treatment of phthalimide **14** with hydrazine monohydrate released the corresponding amine, which was isolated as hydrochloride **15** in 82% yield. After protection of the amine as carbamate **16** (quant. yield), the benzyl protecting-group was cleaved by hydrogenation to give phenol **17** quantitatively. Phenol **17** was then deprotonated with sodium hydride and reaction with 5-chloropentyne gave alkynylated ether **18** in 78%. The *tert*-butyloxycarbonyl (Boc)-protecting group was cleaved by treatment with trifluoroacetic acid and resulting amine **19** was treated with chloroacetyl chloride to give amide **20** in 66% yield.

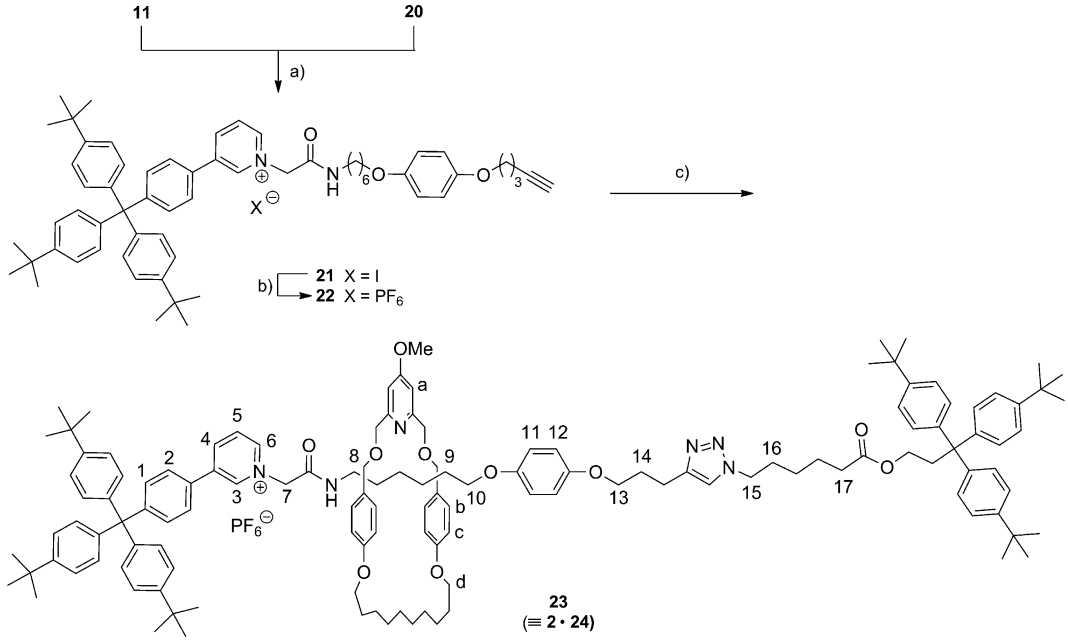
In a Menschutkin reaction, the nitrogen atom of pyridine stopper **11** was alkylated with alkyne linker **20** to give alkyne half-axis **21** in 51%. In this reaction, the positive charge needed as part of the axis in the final shuttle is generated (Figure 1). Finally, the iodide counterion was exchanged by using silver(I) hexafluorophosphate to avoid the reaction of iodide ions with the copper catalyst in the rotaxane-forming 1,3-dipolar cycloaddition reaction.

Rotaxane Assembly

Finally, the rotaxane was synthesized by trapping the two half axes **22** and **7** within macrocycle **2**. Equimolar amounts of alkyne half-axis **22**, azide half-axis **7** and macrocycle **2** were dissolved in dichloromethane and $Cu(CH_3CN)_4PF_6$ was added as catalyst (Scheme 5). Because of strong binding of the copper ions in pyridine macrocycle **2**, the copper catalyst was used in equimolar amounts. After two days of stirring at room temperature, rotaxane **23** and free axis **24** were isolated in 3% and 32% yield, respectively.



Scheme 4. Synthesis of alkyne linker **20**. (a) K_2CO_3, 1,6-dibromohexane, acetone, 21 h, reflux, 69%; (b) potassium phthalimide, DMF, 8 h, 70 °C, 95%; (c) (i) hydrazine monohydrate, CH_2Cl_2, MeOH, 17 h, room temp., (ii) 1 M HCl, 82%; (d) Et_3N, di-*tert*-butyldicarbonate, CH_2Cl_2, 19 h, room temp., quant.; (e) H_2, Pd/C, $CHCl_3$/ethyl acetate (1:1), 22 h, room temp., 100%; (f) 5-chloropentyne, NaH, DMF, 22 h, room temp., 78%; (g) F_3CCOOH, CH_2Cl_2, 21 h, room temp., 92%; (h) chloroacetyl chloride, Et_3N, CH_2Cl_2, 2 h, –10 °C, 66%.



Scheme 5. Synthesis of rotaxane **23** consisting of ring **2** and axis **24**. (a) NaI, 1,4-dioxane, 17 h, reflux, 51%; (b) $AgPF_6$, CH_2Cl_2, 1 h, room temp., 72%; (c) macrocycle **2**, azide half-axis **7**, $Cu^I(CH_3CN)_4PF_6$, CH_2Cl_2, 2 d, room temp., 3% rotaxane, 32% axis.

The MALDI-TOF spectrum gave a peak at *m*/*z* = 1997, which corresponds to the mass of rotaxane **23** without the counterion. Figure 2 shows the NMR spectra of rotaxane **23** and its components, axis **24** and macrocycle **2**. By analysis of the chemically induced shifts in the ^{1}H NMR spectra, the position of the macrocycle could be determined. Owing to the presence of aromatic rings in the macrocycle, the encapsulated part of the axis is shielded and the respective signals are shifted upfield. The shifts clearly show that the preferred position of the macrocycle is close to the pyridinium ion. Two supramolecular interactions favor this orientation: (i) the formation of a hydrogen bond between the amide N–H in the axis and the pyridine nitrogen atom in the macrocycle. (ii) π-π-interactions between the aromatic

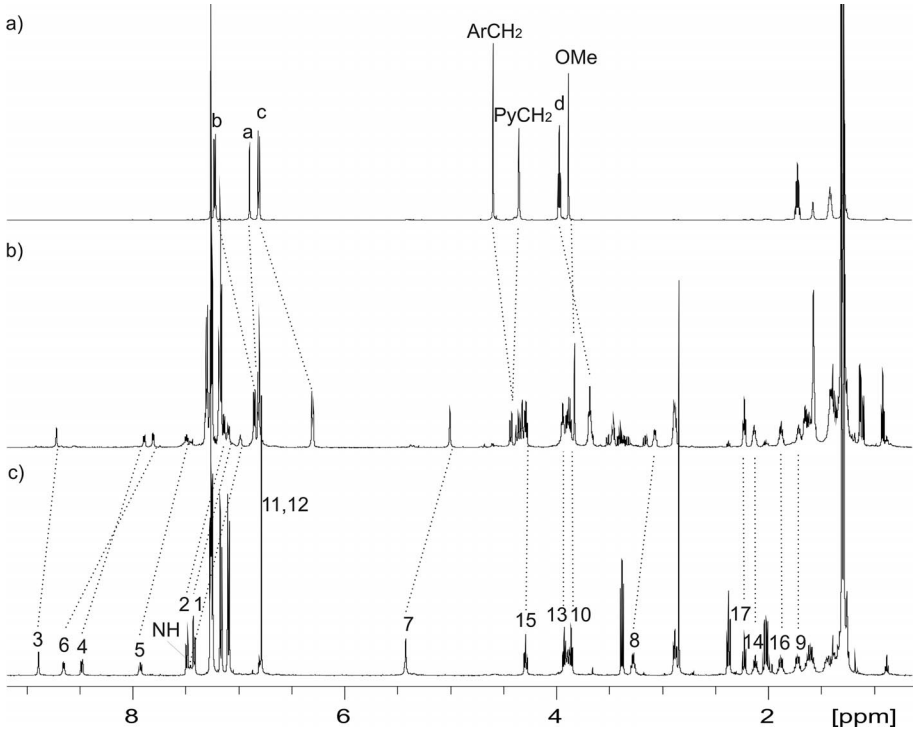


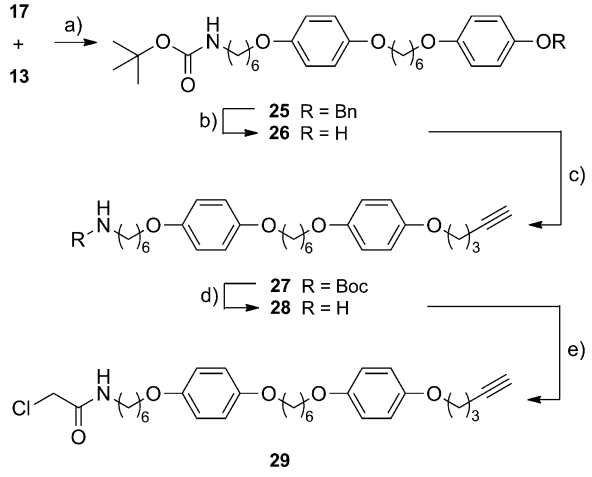
Figure 2. ^{1}H NMR spectra of (a) macrocycle **2**, (b) rotaxane **23** and (c) axis **24** in $CDCl_3$. Protons of the axis are numbered, protons of the ring are labelled with letters. Chemically induced shifts in the rotaxane are indicated by dotted lines.

rings of the macrocycle and the electron poor pyridinium unit of the axis. These interactions also cause shifts of the protons of the aromatic rings in the macrocycle and of a CH_2 group (Figure 2, Label d).

Rotaxane syntheses by the trapping method can lead to very good yields[19] but rotaxane **23** was isolated in only 3%. Two factors may be responsible for this: (i) the high yields of other rotaxanes formed by trapping have been achieved by using an excess of the half axes (in many experiments, a five fold excess was used[19]). In the case of rotaxane **23**, the syntheses of the half axes need more effort. Therefore, they have not been used in excess. (ii) the permanent positive charges of the pyridinium unit and the copper ion are repelling each other, which may cause a yield-diminishing effect. A larger distance between the two ions might lead to a higher yield of a respective rotaxane. Moreover, the total length of rotaxane **23** is quite short. In an application for proton transport across a membrane, the rotaxane must be adjusted to the thickness of the membrane, i.e. 3–4 nm for a typical biological membrane. Therefore, alkyne linker **20** was extended to yield a longer rotaxane and extend the distance between the alkyne function and the pyridinium ion.

Synthesis of the Elongated Alkyne Half-axis

An extended alkyne linker **29** was prepared in five steps, starting from phenol **17** that was used for the synthesis of shorter alkyne linker **20** (Scheme 4). Phenol **17** was deprotonated with sodium hydride and reaction with bromide **13** gave elongated ether **25** in 75% yield. The benzyl protecting-group was cleaved by hydrogenation and free phenol **26** was obtained in 94% yield. Alkylation of the phenol with 5-chloropentyne led to alkyne **27** in 76% yield. By reaction with trifluoroacetic acid, the Boc-protecting group in **27** was cleaved. Resulting amine **28** was treated with chloroacetyl chloride to give amide **29** in 66% yield (Scheme 6).



Scheme 6. Synthesis of the elongated alkyne linker **29**. (a) NaH, DMF, 2 d, room temp., 75%; (b) H_2, Pd/C, $CHCl_3$, 22 h, room temp., 94%; (c) 5-chloropentyne, NaH, DMF, 18 h, room temp., 76%; (d) F_3CCOOH, CH_2Cl_2, 19 h, room temp., 95%; (e) chloroacetyl chloride, Et_3N, CH_2Cl_2, 4 h, room temp., 70%.

Analogous to the formation of short half-axis **21**, elongated alkyne **29** was coupled with pyridine **11** in a Menschutkin reaction. Pyridinium iodide **30** was isolated in 66% yield. Again, the iodide counterion was exchanged by reaction with silver(I) hexafluorophosphate and pyridinium hexafluorophosphate **31** was obtained in 58% yield.

Assembly of the Longer Rotaxane

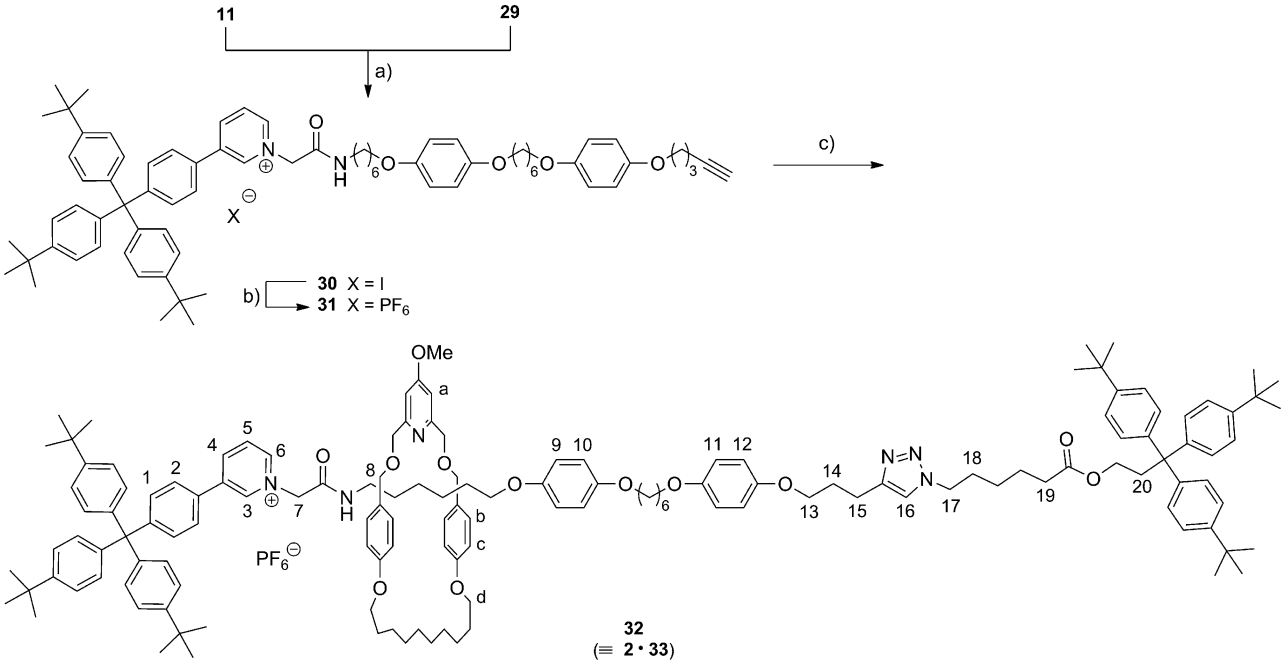
For the synthesis of rotaxane **32**, a mixture of macrocycle **2**, azide half-axis **7**, and elongated alkyne half-axis **31** was stirred with $Cu(CH_3CN)_4PF_6$ in dichloromethane for two days at room temperature. Also in this synthesis, macrocycle **2**, copper catalyst and half-axes **7** and **31** were used in equimolar concentrations. Rotaxane **32** was isolated in 7% yield and the free axis was obtained in 28% yield (Scheme 7).

The MALDI-TOF spectrum of rotaxane **32** has an intensive peak at m/z = 2190, corresponding to the mass of rotaxane **32** without counterion PF_6^-. The elemental composition of the rotaxane was confirmed by HRMS (ICR, see Supporting Information). As shown in Figure 3, analysis of the NMR spectra of rotaxane **32** with macrocycle **2** and free axis **33** confirms the interlocked structure. Furthermore, the position of the macrocycle on the axis could be determined. The spectra look quite similar to those depicted in Figure 2 for shorter rotaxane **23**. Again, the preferred position of the macrocycle is in the vicinity of the pyridinium ion. A 2D NOESY spectrum of rotaxane **32** (see Supporting Information) shows cross signals of the CH_2 group 7 of the axis with the aromatic proton b and the CH_2 group next to the pyridine ($PyCH_2$) of the macrocycle. This supports the assumption that the macrocycle is located close to the pyridinium ion.

The mechanically interlocked structure of rotaxane **32** was also proven by diffusion-ordered nuclear magnetic resonance spectroscopy (DOSY). The diffusion constant of a molecule depends on the molecular mass and the solvodynamic radius of the component. The spectrum in Figure 3 (d) shows that all signals from rotaxane **32** exhibit just one diffusion constant. The diffusion constants for rotaxane **32**, its components axis **33** and ring **2**, and a mixture of the two are listed in Table 1.

Owing to its smaller size, the macrocycle diffuses faster and exhibits a larger diffusion constant. Although rotaxane **32** has a larger molecular weight than free axis **33**, their diffusion constants are extremely similar. In contrast, the diffusion constant of free axis **33** seems to be a little bit smaller than that of rotaxane **32**. But this should not be over interpreted because the magnitude of potential errors is not known. It must be kept in mind that diffusion constants are determined not for naked molecules but for solvated ones. In rotaxane **32**, the positive charge of the rotaxane is shielded from the solvent by the macrocycle. In contrast in free axis **33**, the pyridinium ion can be solvated.

As described in Figure 1, the rotaxane should finally function as a light-driven proton shuttle. Therefore, the



Scheme 7. Synthesis of rotaxane **32** consisting of ring **2** and axis **33**. (a) NaI, 1,4-dioxane, 2 d, reflux, 66%; (b) $AgPF_6$, CH_2Cl_2, 2 h, room temp., 58%; (c) macrocycle **2**, azide half-axis **7**, $Cu^I(CH_3CN)_4PF_6$, CH_2Cl_2, 2 d, room temp., 7% rotaxane, 28% axis.

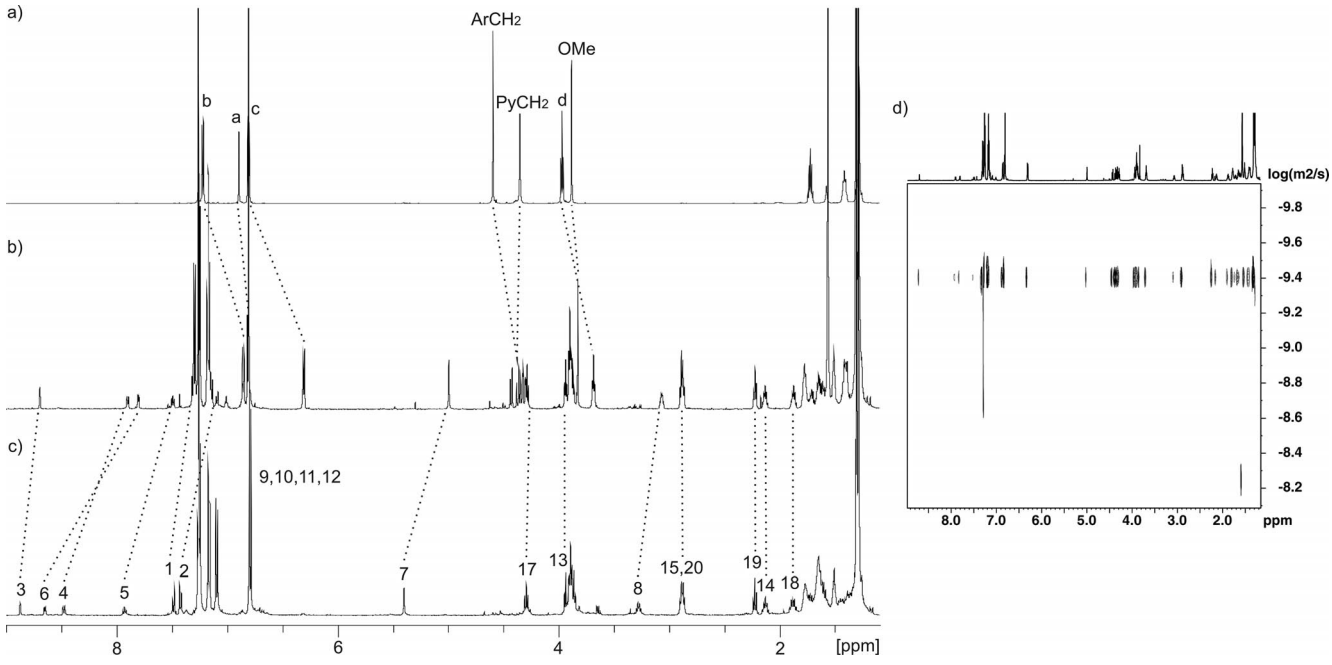


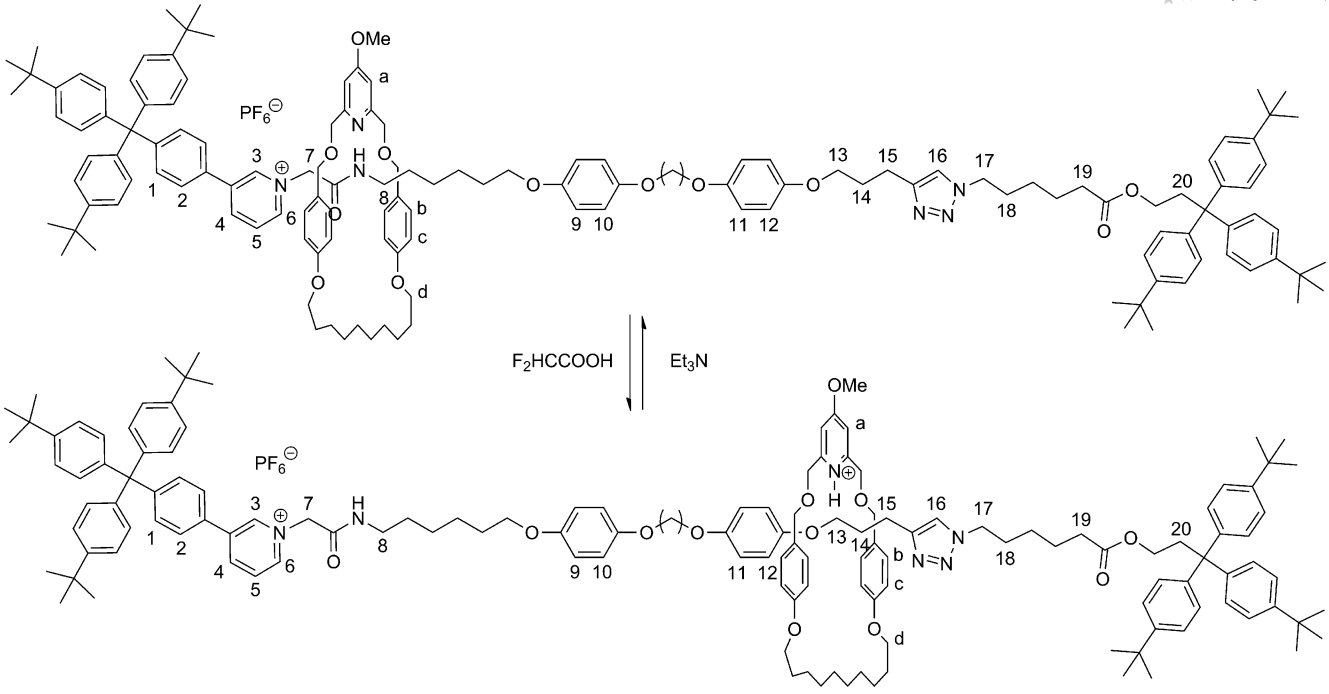
Figure 3. ^1H NMR spectra of (a) macrocycle **2**, (b) rotaxane **32** and (c) free axis **33** in $CDCl_3$. (d) 2D DOSY spectrum of the rotaxane **32** in $CDCl_3$.

Table 1. Diffusion constants *D* for **32**, its components **33** and **2,** and a mixture of the two determined in $CDCl_3$.

	D [10^{-10} m^2s^{-1}] signals for axis	macrocycle
rotaxane **32**	3.62	3.60
axis **33**	3.38	
macrocycle **2**		8.11
axis **33** + macrocycle **2**	3.50	8.04

macrocycle has to move along the axis when the pH changes. The addition of an acid protonates the macrocycle, and as a result of repulsive interactions with the permanent positive charge of the axis, the macrocycle should move along the axis. By addition of a base, the macrocycle is deprotonated and it may diffuse back to the starting position (Scheme 8).

The pH sensitivity of rotaxane **32** was verified by NMR spectroscopy experiments (Scheme 8 and Figure 4). Di-



Scheme 8. Movement of the ring along the axis in rotaxane **32** when acid or base are added.

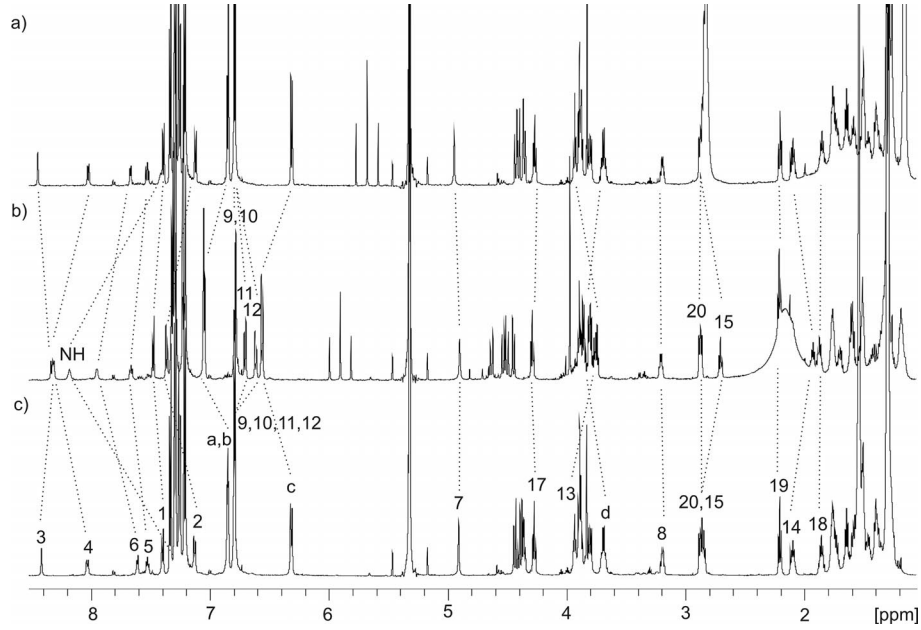


Figure 4. ^{1}H NMR spectra in CD_2Cl_2 of (c) rotaxane **32**, (b) rotaxane **32** upon addition of 3.2 equiv. $F_2HCCOOH$ according to integration and (a) neutralization by the addition of 3.2 equiv. NEt_3 according to integration. Changes are marked with dashed lines. The letters and numbers of the corresponding protons are shown in Scheme 8.

fluoroacetic acid was chosen for two reasons: (i) owing to the remaining hydrogen atom in this fluorinated acetic acid, its concentration can be detected in the NMR spectra, and (ii) in contrast to, for instance *p*-toluenesulfonic acid, this acid is available without water.

Upon addition of difluoroacetic acid to rotaxane **32**, the signal of the pyridine protons of the macrocyclic ring (a) is shifted downfield owing to the protonation of the pyridine nitrogen atom. The shifts of the ring protons b, c and d also changed, indicating a new environment. The protons of the pyridinium ion in the axis (4, 5, 6) and the neighboring aromatic ring (1, 2) are shifted downfield (see Figure 4, c and b). These findings indicate that the macrocycle changes its position on the axis. The upfield shift of protons 11 to 15 of the axis suggest that the macrocycle is now located between the aromatic ring (11, 12) and the triazol. The 2D

NOESY spectrum of protonated rotaxane **32·H$^+$** (see Supporting Information) shows a cross signal between the aromatic protons (b) of the macrocycle and the aromatic protons (12) of the axis. This indicates π–π stacking of the two aromatic rings. Another stabilizing force for this position may be a hydrogen bond between the proton at the nitrogen atom of the pyridinium ion and a triazol nitrogen atom.

Addition of triethylamine leads to deprotonation of the macrocycle (Figure 4, a). Consequently, the macrocycle moves back to the starting position. The NMR spectrum shows that all signals are shifting back to their original positions (see differences between parts a and c in Figure 4).

Conclusions

[2]Rotaxane **32**, which can be switched by protons, has been synthesized. As the basis for this switching process, a permanent positive charge has been incorporated into the axis, and a ring containing a basic center has been chosen. NMR studies in acidic and basic milieus proved that the ring moves along the axis upon protonation. In its unprotonated state, supramolecular interactions, such as a hydrogen bond and π–π interactions, bind the ring on one side of the rotaxane next to the permanent positive charge. Protonation of the ring results in repulsion by Coulomb forces and the protonated ring moves along the axis whereby it will eventually release the proton. Future experiments will aim to modify the stoppers in such a way that the rotaxane is able to span a bilayer membrane.

Experimental Section

General Remarks: The following chemicals were obtained commercially and were used without further purification: 4-benzyloxyphenol (Alfa Aesar), chloroacetyl chloride (Acros), 5-chloropentyne (Acros), $Cu(CH_3CN)_4PF_6$ (Aldrich), 1,6-dibromohexane (Aldrich), 3-(tributylstannyl)pyridine (Maybridge), difluoroacetic acid (ABCR). Macrocycle **1**,[13] 4-[tris(4-*tert*-butylphenyl)methyl]aniline (**8**),[27] 3,3,3-tris(4-*tert*-butylphenyl)propionic acid (**3**),[25] and 6-bromohexanoyl chloride (**5**),[26] were prepared according to literature procedures. Dry solvents were obtained with suitable desiccants. All reactions carried out with dry solvents were performed under nitrogen. Column chromatography was carried out with silica gel (0.04–0.063 mm, Macherey–Nagel). ^{1}H and ^{13}C NMR spectra were recorded with Bruker AC 200, DRX 500 or AV 600 instruments. Assignments are supported by COSY, HSQC spectroscopy, HMBC, and NOESY. Even when obtained by DEPT, the type of ^{13}C signal is always listed as singlet, doublet, etc. All chemical shifts are referenced to tetramethylsilane or to the residual proton or carbon signal of the solvent. Signal assignment in NMR spectra: if there is more than one aromatic ring in a molecule, the rings are labeled Ar^1, Ar^2 and so on from left to right according to the orientation in the schemes above. Mass spectra were recorded with a Finnigan MAT 8200 or MAT 8230. MALDI-TOF mass spectra were recorded with a Bruker-Daltonics Biflex III with Cl-CCA (4-chloro-α-cyano-cinnamic acid) as matrix. ESI mass spectra were recorded with an Applied Biosystems Mariner Spectrometry Workstation. HRMS were recorded with an APEX 3 FT-ICR and a 7.05 T magnet from Bruker Daltonics. IR spectra were recorded with a Perkin–Elmer Spectrum 100 spectrometer equipped with a MKII Golden GateTM Single Reflection ATR unit. Elemental analyses were carried out with a Euro EA 3000 Elemental Analyzer from Euro Vector.

5^4-Methoxy-3,7,10,21-tetraoxa-1,9(1,4)-dibenzena-5(2,6)-pyridinacycloheneicosaphan (2): Hydrogen was bubbled through a suspension of platinum oxide (3.8 mg, 17 μmol) in acid-free chloroform for 30 min. A solution of macrocycle **1**[13] (101 mg, 195 μmol) in acid-free chloroform (10 mL) was added, and the mixture was flushed with hydrogen for further 1.5 h, followed by stirring for 2 d under hydrogen. The solvent was evaporated and the residue was purified by column chromatography (silica gel, dichloromethane/ethyl acetate, 1:1, R_f = 0.54) to afford compound **2** as a white solid (101 mg, 99%); m.p. 104 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22 (d, ^3J = 8.6 Hz, 4 H, Ar-3,5-H), 6.90 (br. s, 2 H, Py-3,5-H), 6.80 (d, ^3J = 8.6 Hz, 4 H, Ar-2,6-H), 4.59 (s, 4 H, ArCH_2), 4.37 (br. s, 4 H, PyCH_2), 3.97 (t, ^3J = 6.4 Hz, 4 H, ArOCH_2), 3.89 (s, 3 H, OCH_3), 1.72 (quint, ^3J = 6.7 Hz, 4 H, OCH_2CH_2), 1.45–1.37 [m, 4 H, $O(CH_2)_2CH_2$], 1.32–1.24 [m, 8 H, $O(CH_2)_3CH_2CH_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.3 (s, Py-*C*-4)*, 158.8 (s, Ar-*C*-1), 130.1 (d, Ar-*C*-3,5), 129.2 (s, Ar-*C*-4), 114.7 (d, Ar-*C*-2,6), 105.9 (d, Py-*C*-3,5), 72.3 (t, Ar*C*H_2), 71.0 (t, Py*C*H_2), 67.4 (t, ArO*C*H_2), 29.4, 28.7 [2t, $O(CH_2)_3CH_2CH_2$], 28.6 (t, OCH_2CH_2), 25.7 [t, $O(CH_2)_2CH_2$] ppm. *The signal was only detected in the HMBC spectrum. The quaternary Py-*C*-2,6-signal could not be detected in the ^{13}C NMR spectrum. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 520 $[M + H]^+$.

1-Iodo-4-[tris(4-*tert*-butylphenyl)methyl]benzene (9): A suspension of 4-[tris(4-*tert*-butylphenyl)methyl]aniline[27] (**8**; 2.52 g, 5.00 mmol) in a mixture of acetone (50 mL) and conc. hydrochloric acid (12 mL) was cooled to 0 °C and a solution of sodium nitrite (535 mg, 7.76 mmol) in water (3.5 mL) was added. The suspension was stirred for 30 min at 0 °C and then potassium iodide (1.34 g, 8.10 mmol) in water (5 mL) was added. The reaction mixture was stirred for 1 h at 0 °C, followed by 1 h at room temperature and finally 2 h at 60 °C. The reaction mixture was treated with a 48% aqueous sodium hydrogen sulfite solution (100 mL) and neutralized with a saturated aqueous sodium hydrogen carbonate solution. The solution was extracted with diethyl ether (3 × 50 mL), the combined organic layers were washed with water (100 mL) and brine (2 × 50 mL) and finally dried with magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, dichloromethane/methanol, 10:1, R_f = 0.83) to give **9** as a pale yellow solid (2.09 g, 68%); m.p. 308 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54 (d, ^3J = 8.7 Hz, 2 H, Ar-3,5-H), 7.23 (d, ^3J = 8.7 Hz, 6 H, *t*BuAr-3,5-H), 7.06 (d, ^3J = 8.7 Hz, 6 H, *t*BuAr-2,6-H), 6.95 (d, ^3J = 8.7 Hz, 2 H, Ar-2,6-H), 1.30 (s, 27 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.6 (s, *t*BuAr-*C*-4), 147.3 (s, Ar-*C*-1), 143.4 (s, *t*BuAr-*C*-1), 136.3 (d, Ar-*C*-3,5), 133.5 (d, Ar-*C*-2,6), 130.6 (d, *t*BuAr-*C*-2,6), 124.2 (d, *t*BuAr-*C*-3,5), 91.5 (s, Ar-*C*-4), 63.5 [s, *C*(*t*BuAr)$_3$], 34.3 [s, $C(CH_3)_3$], 31.3 (q, CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3032 (arom. C–H), 2960, 2903, 2867 (aliph. C–H), 1505, 1479, 1460 (arom.), 843, 823 (1,4-disubstitution) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 614 (45) $[M]^{+\cdot}$, 557 (14) $[M - C(CH_3)_3]^+$, 481 (100) $[M - C_6H_4C(CH_3)_3]^+$, 411 (82) $[M - C_6H_4I]^+$, 355 (26) $[M - C_6H_4C(CH_3)_3 - I]^+$. $C_{37}H_{43}I$ (614.24): C 72.30, H 7.05. $C_{37}H_{43}I{\cdot}1CH_2Cl_2{\cdot}2CH_3OH$ (762.25): calcd. C 60.20, H 6.57; found C 60.47, H 6.23.

1-Bromo-4-[tris(4-*tert*-butylphenyl)methyl]benzene (10): A mixture of 4-[tris(4-*tert*-butylphenyl)methyl]aniline[27] (**8**; 1.49 g, 2.96 mmol) and 48% aqueous hydrobromic acid (4.37 mL, 38.7 mmol) in acetone (50 mL) was cooled to 0 °C. A solution of sodium nitrite

(292 mg, 4.17 mmol) in water (4 mL) was added and the mixture was stirred at 0 °C for 1 h. A solution of copper(I)bromide (748 mg, 5.21 mmol) in aqueous hydrobromic acid (48% ,1 mL) was added and the reaction mixture was stirred for 3 h at room temperature. The precipitate was filtered and washed with water (20 mL) and dichloromethane (20 mL). After separation of the phases, the aqueous layer was extracted with dichloromethane (3 × 40 mL) and the combined organic layer was washed with brine (50 mL) and dried with magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, dichloromethane/cyclohexane, 1:1, R_f = 0.83) to give **10** as a light orange solid (875 mg, 52%); m.p. 278 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34 (d, ^3J = 8.7 Hz, 2 H, Ar-2,6-H), 7.23 (d, ^3J = 8.7 Hz, 6 H, *t*BuAr-3,5-H), 7.08 (d, ^3J = 8.7 Hz, 2 H, Ar-3,5-H), 7.06 (d, ^3J = 8.7 Hz, 6 H, *t*BuAr-2,6-H), 1.30 [s, 27 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.6 (s, *t*BuAr-*C*-4), 146.6 (s, Ar-*C*-4), 143.4 (s, *t*BuAr-*C*-1), 133.0 (d, Ar-*C*-3,5), 130.6 (d, *t*BuAr-*C*-2,6), 130.3 (d, Ar-*C*-2,6), 124.2 (d, *t*BuAr-*C*-3,5), 119.8 (s, Ar-*C*-1), 63.4 [s, *C*(*t*BuAr)$_3$], 34.3 [*C*(CH$_3$)$_3$], 31.4 [q, C(*C*H$_3$)$_3$] ppm. IR (ATR): $\tilde{\nu}$ = 2960, 2904, 2867 (aliph. C–H), 1506 (C=C), 823 (1,4-disubstitution) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 568, 566 (27, 25) [M]$^{+\cdot}$, 511, 509 (7, 5) [M – CH$_3$]$^+$, 488 (40) [M – Br – H]$^{+\cdot}$, 435, 433 (74, 87) [M – C$_{10}$H$_{13}$]$^+$, 411 (100) [M – C$_6$H$_4$Br]$^+$. MS (CI, isobutane): *m*/*z* (%) = 568, 566 (9, 8) [M]$^{+\cdot}$, 435, 433 (100, 97) [M – C$_{10}$H$_{13}$]$^+$.

3-{4-[Tris(4-*tert*-butylphenyl)methyl]phenyl}pyridine (11): Method A: A mixture of 1-iodo-4-[tris(4-*tert*-butylphenyl)methyl]benzene (**9**, 641 mg, 1.04 mmol), 3-(tributyltin)pyridine (500 µL, 577 mg, 1.56 mmol), bis(triphenylphosphine)palladium(II)chloride (92.6 mg, 132 µmol) and copper(I)iodide (65.9 mg, 347 µmol) in anhydrous dimethylformamide (DMF) was heated for 20 h at 100 °C. Then, the reaction mixture was cooled to room temperature and dichloromethane (40 mL) and water (40 mL) were added. After separation of the layers, the aqueous layer was extracted with dichloromethane (50 mL) and the combined organic layer was washed with water (40 mL) and brine (40 mL) and dried with magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 6:1, R_f = 0.17) to obtain **11** as a white solid (222 mg, 38%). **Method B:** A mixture of 1-bromo-4-[tris(4-*tert*-butylphenyl)methyl]benzene (**10**, 400 mg, 706 µmol), 2-(3-pyridyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan (175 mg, 853 µmol), barium hydroxide octahydrate (495 mg, 1.57 mmol), palladium(II)-acetate (16.4 mg, 73.1 µmol) and 1,3-bis(diphenylphosphanyl)propane (62.1 mg, 151 µmol) in 1,2-dimethoxyethane (DME; 36 mL) and water (9 mL) was heated to reflux for 24 h. The reaction mixture was cooled to room temperature and dichloromethane (50 mL) and water (50 mL) were added. After separation of the layers, the aqueous layer was extracted with dichloromethane (3 × 50 mL) and the combined organic layer was washed with brine (70 mL) and dried with magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 6:1, R_f = 0.17) to obtain **11** as a white solid (106 mg, 26%); m.p. > 330 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.86 (m$_c$, 1 H, Py-2-H), 8.55 (dd, ^3J = 4.8, ^4J = 1.6 Hz, 1 H, Py-6-H), 7.87 (ddd, ^3J = 7.9, ^4J = 2.3, ^4J = 1.6 Hz, 1 H, Py-4-H), 7.47 (d, ^3J = 8.6 Hz, 2 H, PyAr-2,6-H), 7.36–7.33 (m, 1 H, Py-5-H), 7.32 (d, ^3J = 8.6 Hz, 2 H, PyAr-3,5-H), 7.26 (d, ^3J = 8.7 Hz, 6 H, *t*BuAr-3,5-H), 7.13 (d, ^3J = 8.7 Hz, 6 H, *t*BuAr-2,6-H), 1.31 (s, 27 H, C*H*$_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.6 (s, *t*BuAr-*C*-4), 148.2 (d, Py-*C*-2, Py-*C*-6), 147.6 (s, PyAr-*C*-4), 143.7 (s, *t*BuAr-*C*-1), 136.3 (s, Py-*C*-3), 134.8 (s, PyAr-*C*-1), 134.1 (d, Py-*C*-4), 132.0 (d, PyAr-*C*-3,5), 130.7 (d, *t*BuAr-*C*-2,6), 125.8 (d, PyAr-*C*-2,6), 124.2 (d, *t*BuAr-*C*-3,5), 123.5 (d, Py-*C*-5), 63.6 [s, *C*(*t*BuAr)$_3$], 34.3 [s, *C*(CH$_3$)$_3$], 31.4 (q, *C*H$_3$) ppm. IR (ATR): $\tilde{\nu}$ = 2957, 2866 (aliph. C–H), 1684 (C=N), 1505 (C=C), 824 (1,4-disubstitution), 799, 708 (monosubstitution) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 565 (65) [M]$^{+\cdot}$, 508 (28) [M – C$_4$H$_9$]$^+$, 433 (100) [M – C$_{10}$H$_{12}$]$^{+\cdot}$, 411 (74) [M – C$_{11}$H$_8$N]$^+$. MS (MALDI-TOF): *m*/*z* = 566 [M + H]$^+$. $C_{42}H_{47}N$ (565.37): C 89.15, H 8.37, N 2.48. $C_{42}H_{47}N\cdot0.75H_2O$ (578.88): calcd. C 87.07, H 8.44, N 2.42; found C 86.92, H 8.45, N 2.41.

3,3,3-Tris(4-*tert*-butylphenyl)propanol (4): A mixture of 3,3,3-tris(4-*tert*-butylphenyl)propionic acid[25] (**3**, 5.64 g, 12.0 mmol) and thionyl chloride (30 mL) was heated to reflux for 2 h. The excess thionyl chloride was removed under reduced pressure and toluene (100 mL) was added. The solvent was removed by distillation and the residue was dissolved in anhydrous diethyl ether. A solution of lithium aluminum hydride (912 mg, 24.0 mmol) in anhydrous diethyl ether (60 mL) was added and the mixture was heated to reflux for 2 h. The mixture was hydrolyzed by the addition of water and hydrochloric acid (1 M). After separation of the layers, the aqueous layer was extracted with diethyl ether (3 × 100 mL). The combined organic layer was washed with saturated aqueous sodium hydrogen carbonate solution (50 mL) and water (50 mL) and dried with magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by crystallization from cyclohexane to obtain **4** as a white solid (3.86 g, 71%). 205 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.26 (d, ^3J = 8.7 Hz, 6 H, *t*BuAr-2,6-H), 7.17 (d, ^3J = 8.7 Hz, 6 H, *t*BuAr-3,5-H), 3.50 (t, ^3J = 7.1 Hz, 2 H, C*H*$_2$CH$_2$OH), 2.87 (t, ^3J = 7.1 Hz, 2 H, CH$_2$C*H*$_2$OH), 1.29 [s, 27 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 148.5 (s, *t*BuAr-*C*-4), 144.2 (s, *t*BuAr-*C*-1), 128.5 (d, *t*BuAr-*C*-3,5), 124.7 (d, *t*BuAr-*C*-2,6), 60.8 (t, *C*H$_2$OH), 54.1 [s, (*t*BuAr)$_3$*C*], 43.1 (t, *C*H$_2$CH$_2$OH), 34.3 [s, *C*(CH$_3$)$_3$], 31.4 [q, C(*C*H$_3$)$_3$] ppm. IR (ATR): $\tilde{\nu}$ = 3326 (OH), 3032 (arom. C–H), 2959, 2927, 2903 (aliph. C–H), 1507, 1459 (arom. C–H), 1015 (C–O), 841, 820 (1,4-disubstitution) cm^{-1}. MS (ESI, MeOH): *m*/*z* (%) = 479 (25) [M + Na]$^+$, 437 (30) [M – OH]$^+$. $C_{33}H_{44}O$ (456.70): C 86.79, H 9.71. $C_{33}H_{44}O\cdot C_6H_{12}$ (540.86): calcd. C 86.61, H 10.44; found C 86.37, H 10.81.

[3,3,3-Tris(4-*tert*-butylphenyl)]propyl 6-Bromohexanoate (6): 3,3,3-Tris(4-*tert*-butylphenyl)propanol (**4**, 1.12 g, 2.45 mmol) was dissolved in anhydrous dichloromethane (25 mL), and anhydrous triethylamine (407 µL, 297 mg, 2.94 mmol) and 6-bromohexanoic acid chloride (**5**, 676 mg, 319 mmol) were added. The reaction mixture was heated to reflux for 19 h and washed with brine (2 × 30 mL) afterwards. The organic layer was dried with magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 6:1, R_f = 0.60) and **6** was obtained as a white solid (1.26 g, 81%); m.p. 158 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (d, ^3J = 8.7 Hz, 6 H, *t*BuAr-2,6-H), 7.17 (d, ^3J = 8.7 Hz, 6 H, *t*BuAr-3,5-H), 3.91 (m$_c$, 2 H, COOC*H*$_2$), 3.40 (t, ^3J = 6.8 Hz, 2 H, C*H*$_2$Br), 2.89 (m$_c$, 2 H, COOCH$_2$C*H*$_2$), 2.25 (t, ^3J = 7.4 Hz, 2 H, C*H*$_2$COOCH$_2$), 1.87 (m$_c$, 2 H, C*H*$_2$CH$_2$Br), 1.62 (m$_c$, 2 H, C*H*$_2$CH$_2$COO), 1.50–1.40 [m, 2 H, C*H*$_2$(CH$_2$)$_2$Br], 1.29 [s, 27 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.5 (s, *C*OO), 148.5 (s, *t*BuAr-*C*-4), 143.8 (s, *t*BuAr-*C*-1), 128.5 (d, *t*BuAr-*C*-2,6), 124.7 (d, *t*BuAr-*C*-3,5), 62.9 (t, COO*C*H$_2$), 53.7 [s, (*t*BuAr)$_3$*C*], 38.8 (t, COOCH$_2$*C*H$_2$), 34.3 [s, *C*(CH$_3$)$_3$], 34.0 (t, *C*H$_2$COOCH$_2$), 33.5 (t, *C*H$_2$Br), 32.4 (t,*C*H$_2$CH$_2$Br), 31.4 [q, C(*C*H$_3$)$_3$], 27.6 [t, *C*H$_2$(CH$_2$)$_2$Br], 24.0 (t,*C*H$_2$CH$_2$COO) ppm. IR (ATR): $\tilde{\nu}$ = 3032 (arom. C–H), 2992, 2959, 2866 (aliph. C–H), 1733 (C=O), 1508, 1460 (arom.), 1015 (C–O), 841, 820 (1,4-disubstitution) cm^{-1}. MS (ESI, $CHCl_3$, MeOH): *m*/*z* = 657, 655 [M +

Na]$^+$. $C_{39}H_{53}BrO_2$ (633.74): C 73.91, H 8.43. $C_{39}H_{53}BrO_2 \cdot 0.2C_6H_{12}$ (650.57): calcd. C 74.22, H 8.58; found C 74.39, H 8.75.

[3,3,3-Tris(4-*tert*-butylphenyl)]propyl 6-Azidohexanoate (7): To a solution of bromo ester **6** (978 mg, 1.55 mmol) in DMF (50 mL), sodium azide (503 mg, 7.73 mmol) was added and the reaction mixture was heated to 80 °C for 2 d. Then, water (30 mL) was added and the mixture was extracted with ethyl acetate (2× 40 mL). The combined organic layer was washed with water (40 mL) and brine (2× 50 mL) and dried with magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 5:1, R_f = 0.61) to give **6** as a white solid (822 mg, 89%); m.p. 137 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 (d, ^3J = 8.7 Hz, 6 H, *t*BuAr-3,5-H), 7.17 (d, ^3J = 8.7 Hz, 6 H, *t*BuAr-2,6-H), 3.91 (m_c, 2 H, COOCH_2), 3.27 (t, ^3J = 6.9 Hz, 2 H, CH_2N$_3$), 2.89 (m_c, 2 H, COOCH$_2$CH_2), 2.25 (t, ^3J = 7.5 Hz, 2 H, CH_2COO), 1.66–1.57 (m, 4 H, CH_2CH$_2$COO, CH_2CH$_2$N$_3$), 1.42–1.35 [m, 2 H, CH_2(CH$_2$)$_2$N$_3$], 1.29 [s, 27 H, C(CH_3)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.5 (s, *C*OO), 148.5 (s, *t*BuAr-*C*-4), 143.8 (s, *t*BuAr-*C*-1), 128.5 (d, *t*BuAr-*C*-2,6), 124.7 (d, *t*BuAr-*C*-3,5), 62.9 (t, COO*C*H$_2$), 53.7 [s, (*t*BuAr)$_3$*C*], 51.2 (t, *C*H$_2$N$_3$), 38.7 (t, COOCH$_2$*C*H$_2$), 34.3 [s, *C*(CH$_3$)$_3$], 34.1 (t, *C*H$_2$COO), 31.3 [q, C(*C*H$_3$)$_3$], 28.6 (t, *C*H$_2$CH$_2$N$_3$), 26.2 [t, *C*H$_2$(CH$_2$)$_2$N$_3$], 24.4 (t, *C*H$_2$CH$_2$COO) ppm. IR (ATR): $\tilde{\nu}$ = 3031 (arom. C–H), 2959, 2925, 2851 (aliph. C–H), 2094 (N$_3$), 1735 (C=O), 1508, 1449 (arom.), 1016 (C–O), 841, 820 (1,4-disustitution) cm^{-1}. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 634 [M + K]$^+$, 618 [M + Na]$^+$, 568 [M – N$_2$ + H]$^+$, 411 [$C_{31}H_{39}$]$^+$. $C_{39}H_{53}N_3O_2$ (595.41): calcd. C 78.61, H 8.97, N 7.05; found C 78.56, H 8.99, N 6.54.

1-(Benzyloxy)-4-(6-bromohexyloxy)benzene (13): 1,6-Dibromohexane (19.4 g, 80.0 mmol) was added to a suspension of 4-benzyloxyphenol (8.00 g, 40.0 mmol) and anhydrous potassium carbonate (8.29 g, 60.0 mmol) in anhydrous acetone (80 mL), and the reaction mixture was heated to reflux for 21 h. The mixture was cooled and dichloromethane (100 mL) was added. The precipitate was filtered and washed with dichloromethane (100 mL). The filtrate was concentrated under reduced pressure and the residue was crystallized from *n*-hexane to give **13** as a white solid (10.0 g, 69%); m.p. 76 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, ^3J = 7.3 Hz, 2 H, Bn-2,6-H), 7.37 (t, ^3J = 7.3 Hz, 2 H, Bn-3,5-H), 7.31 (t, ^3J = 7.3 Hz, 1 H, Bn-4-H), 6.90 (d, ^3J = 9.3 Hz, 2 H, Ar-2,6-H), 6.82 (d, ^3J = 9.3 Hz, 2 H, Ar-3,5-H), 5.01 (s, 2 H, BnCH_2), 3.90 (t, ^3J = 6.4 Hz, 2 H, OCH_2), 3.41 (t, ^3J = 6.8 Hz, 2 H, BrCH_2), 1.89 (quint, ^3J = 7.0 Hz, 2 H, BrCH$_2$CH_2), 1.77 (quint, ^3J = 6.8 Hz, 2 H, OCH$_2$CH_2), 1.53–1.41 [m, 4 H, O(CH$_2$)$_2$(CH)$_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.4 (s, Ar-*C*-4), 152.9 (s, Ar-*C*-1), 137.3 (s, Bn-*C*-1), 128.5 (d, Bn-*C*-3,5), 127.9 (d, Bn-*C*-4), 127.5 (d, Bn-*C*-2,6), 115.8 (d, Ar-*C*-3,5), 115.4 (d, Ar-*C*-2,6), 70.7 (t, Bn*C*H$_2$), 68.3 (t, O*C*H$_2$), 33.7 (t, Br*C*H$_2$), 32.7 (t, BrCH$_2$*C*H$_2$), 29.2 (t, OCH$_2$*C*H$_2$), 27.9 [t, (OCH$_2$)$_3$*C*H$_2$], 25.3 [t, (OCH$_2$)$_2$*C*H$_2$] ppm. IR (ATR): $\tilde{\nu}$ = 3043 (arom. C–H), 2937, 2863 (aliph. C–H), 1505 (C=C), 1455, 1467 (C–H), 1224 (C–O), 824 (1,4-disubstitution), 736, 693 (monosubstitution), 645 (C–Br) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 364, 362 (99, 100) [M]$^{+\cdot}$, 273, 271 (6, 9) [M – CH$_2$C$_6$H$_5$]$^+$, 165, 163, (18, 17) [C_6H_{12}Br]$^+$. MS (CI, isobutane): *m*/*z* (%) = 365, 363 (97, 100) [M + H]$^+$, 165, 163 (63, 69) [C_6H_{12}Br]$^+$. $C_{19}H_{23}BrO_2$ (363.29): calcd. C 62.82, H 6.38; found C 62.80, H 6.47.

***N*-[6-(4-Benzyloxyphenyloxy)hexyl]phthalimide (14):** A solution of bromide **13** (1.53 g, 4.24 mmol) and potassium phthalimide (952 mg, 5.13 mmol) in anhydrous DMF was heated at 70 °C for 8 h. The solvent was removed under reduced pressure and dichloromethane was added. The precipitate was filtered and washed with dichloromethane. The filtrate was concentrated under reduced pressure and purified by column chromatography (silica gel, dichloromethane, R_f = 0.56) to obtain the product **14** as a white solid (1.75 g, 95%); m.p. 94 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.83 (m_c, 2 H, Phth-3,6-H), 7.70 (m_c, 2 H, Phth-4,5-H), 7.43–7.40 (m, 2 H, Bn-2,6-H), 7.39–7.34 (m, 2 H, Bn-3,5-H), 7.33–7.28 (m, 1 H, Bn-4-H), 6.88 (d, ^3J = 9.2 Hz, 2 H, Ar-3,5-H), 6.80 (d, ^3J = 9.2 Hz, 2 H, Ar-2,6-H), 5.00 (s, 2 H, Bn-CH_2), 3.89 (t, ^3J = 6.4 Hz, 2 H, OCH_2), 3.69 (t, ^3J = 7.3 Hz, 2 H, NCH_2), 1.79–1.67 (m, 4 H, OCH$_2$CH_2, NCH$_2$CH_2), 1.54–1.46 [m, 2 H, O(CH$_2$)$_2$CH_2], 1.45–1.37 [m, 2 H, N(CH$_2$)$_2$CH_2] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.4 (s, *C*ON), 153.4 (s, Ar-*C*-1), 152.9 (s, Ar-*C*-4), 137.4 (s, Bn-*C*-1), 133.8 (d, Phth-*C*-4,5), 132.2 (s, Phth-*C*-1,2), 128.5 (d, Bn-*C*-3,5), 127.8 (d, Bn-*C*-4), 127.4 (d, Bn-*C*-2,6), 123.2 (d, Phth-*C*-3,6), 115.8 (d, Ar-*C*-3,5), 115.4 (d, Ar-*C*-2,6), 70.7 (t, Bn-*C*H$_2$), 68.4 (t, O*C*H$_2$), 37.9 (t, N*C*H$_2$), 29.1 (t, OCH$_2$*C*H$_2$), 28.5 (t, NCH$_2$*C*H$_2$), 26.6 [t, N(CH$_2$)$_2$*C*H$_2$], 25.7 [t, O(CH$_2$)$_2$*C*H$_2$] ppm. IR (ATR): $\tilde{\nu}$ = 2937 (aliph. C–H), 1774, 1706 (imide, five membered ring, C=O), 1510 (C=C), 1231, 1043 (C–O), 817 (1,4-disubstitution), 744, 700 (monosubstitution) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 429 (54) [M]$^{+\cdot}$, 230 (34) [M – OC$_6$H$_4$OCH$_2$C$_6$H$_5$]$^+$, 160 (100) [$C_9H_6NO_2$]$^+$. MS (CI, isobutane): *m*/*z* (%) = 430 (43) [M + H]$^+$, 230 (100) [M – OC$_6$H$_4$OCH$_2$C$_6$H$_5$]$^+$, 160 (31) [$C_9H_6NO_2$]$^+$. $C_{27}H_{27}NO_4$ (429.19): calcd. C 75.50, H 6.34, N 3.26; found C 75.41, H 6.34, N 3.33.

6-(4-Benzyloxyphenyloxy)hexylamine Hydrochloride (15): Phthalimide **14** (1.00 g, 2.33 mmol) was dissolved in a mixture of dichloromethane (13 mL) and methanol (13 mL), and hydrazine monohydrate (650 µL, 670 mg, 13.4 mmol) was added dropwise. The mixture was stirred for 17 h at room temperature and the precipitate was filtered and washed with dichloromethane (20 mL). The solvent was removed under reduced pressure, a mixture of chloroform (15 mL) and ethyl acetate (15 mL) was added and a precipitate occurred. The precipitate was filtered and the solvent was removed under reduced pressure. Chloroform (30 mL) was added and the organic layer was washed with water (2× 20 mL) and brine (20 mL). The organic layer was concentrated under reduced pressure to 5 mL and hydrochloric acid (1 M) was added and stirred until a pH of 2 was reached. The precipitate was filtered off and washed with cold water, ethyl acetate and diethyl ether and then dried to yield the compound **15** as a white solid (637 mg, 82%); m.p. 196 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.98 (br. s, 3 H, NH_3^+), 7.42 (d, ^3J = 7.3 Hz, 2 H, Bn-2,6-H), 7.38 (t, ^3J = 7.5 Hz, 2 H, Bn-3,5-H), 7.31 (t, ^3J = 7.2 Hz, 1 H, Bn-4-H), 6.92 (d, ^3J = 9.1 Hz, 2 H, Ar-3,5-H), 6.84 (d, ^3J = 9.1 Hz, 2 H, Ar-2,6-H), 5.03 (s, 2 H, Bn-CH_2), 3.88 (t, ^3J = 6.5 Hz, 2 H, OCH_2), 2.75 [sext, ^3J = 6.8 Hz, 2 H, O(CH$_2$)$_5$CH_2NH$_3^+$], 1.67 (quint, ^3J = 6.8 Hz, 2 H, OCH$_2$CH_2), 1.57 [quint, ^3J = 7.4 Hz, 2 H, O(CH$_2$)$_4$-CH_2], 1.45–1.31 [m, 4 H, O(CH$_2$)$_2$(CH_2)$_2$] ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 153.3 (s, Ar-*C*-1), 152.7 (s, Ar-*C*-4), 137.9 (s, Bn-*C*-1), 128.8 (d, Bn-*C*-3,5), 128.2 (d, Bn-*C*-4), 128.0 (d, Bn-*C*-2,6), 116.2 (d, Ar-*C*-3,5), 115.7 (d, Ar-*C*-2,6), 70.1 (t, Bn-*C*H$_2$), 68.1 (t, O*C*H$_2$), 39.1 [t, O(CH$_2$)$_5$*C*H$_2$NH$_3^+$], 29.1 (t, OCH$_2$*C*H$_2$), 27.3 [t, O(CH$_2$)$_4$*C*H$_2$], 26.0, 25.5 [2t, O(CH$_2$)$_2$-(*C*H$_2$)$_2$] ppm. IR (ATR): $\tilde{\nu}$ = 3030 (NH$_3^+$), 2934, 2866 (aliph. C–H), 1598, 1533, 1506 (C=C), 1239, 1012 (C–O), 821 (1,4-disubstitution), 741, 693 (monosubstitution) cm^{-1}. MS (CI, isobutane): *m*/*z* = 300 [M – Cl]$^+$. MS (ESI, MeOH): *m*/*z* = 300 [M – Cl]$^+$. $C_{19}H_{26}ClNO_2$ (335.67): calcd. C 67.94, H 7.80, N 4.17; found C 68.02, H 7.83, N 4.14.

***tert*-Butyl-*N*-6-[4-(benzyloxy)phenyloxy]hexylcarbamate (16):** To a solution of amino chloride **15** (1.16 g, 3.46 mmol) in anhydrous dichloromethane (20 mL), anhydrous triethylamine (1.23 mL, 897 mg, 8.86 mmol) was added. The solution was stirred for 20 min

at room temperature and a solution of di-*tert*-butyldicarbonate (972 mg, 4.57 mmol) in anhydrous dichloromethane (6 mL) was added. The mixture was stirred for 19 h at room temperature and afterwards the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, dichloromethane, R_f = 0.28) to give **16** as a white solid (1.38 g, quant.); m.p. 93 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 (d, ^3J = 7.3 Hz, 2 H, Bn-2,6-H), 7.37 (t, ^3J = 7.6 Hz, 2 H, Bn-3,5-H), 7.31 (t, ^3J = 7.3 Hz, 1 H, Bn-4-H), 6.89 (d, ^3J = 9.1 Hz, 2 H, Ar-3,5-H), 6.81 (d, ^3J = 9.1 Hz, 2 H, Ar-2,6-H), 5.01 (s, 2 H, Bn-CH_2), 4.51 (br. s, 1 H, N*H*), 3.89 (t, ^3J = 6.5 Hz, 2 H, OCH_2), 3.12 (m_c, 2 H, NHCH_2), 1.75 (quint, ^3J = 7.0 Hz, 2 H, OCH$_2$CH_2), 1.53–1.45 [m, 4 H, HNCH$_2$CH_2, O(CH$_2$)$_2$CH_2], 1.44 (s, 9 H, CH_3), 1.41–1.33 [m, 2 H, NH(CH$_2$)$_2$CH_2] ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 156.0 (s, *C*ONH), 153.4 (s, Ar-*C*-1), 152.9 (s, Ar-*C*-4), 137.3 (s, Bn-*C*-1), 128.5 (d, Bn-*C*-3,5), 127.9 (d, Bn-*C*-4), 127.5 (d, Bn-*C*-2,6), 115.8 (d, Ar-*C*-3,5), 115.4 (d, Ar-*C*-2,6), 79.0 [s, *C*(CH$_3$)$_3$], 70.7 (t, Bn-*C*H$_2$), 68.4 (t, O*C*H$_2$), 40.5 (t, NH*C*H$_2$), 30.0 (t, NHCH$_2$*C*H$_2$), 29.3 (t, OCH$_2$*C*H$_2$), 28.4 (q, *C*H$_3$), 26.6 [t, NH(CH$_2$)$_2$*C*H$_2$], 25.8 [t, O(CH$_2$)$_2$*C*H$_2$] ppm. IR (ATR): $\tilde{\nu}$ = 3389 (N–H), 2935, 2867 (aliph. C–H), 1686 (C=O), 1520 (N–H), 1510 (C=C), 1235, 1166 (C–O), 816 (1,4-disubstitution), 741, 699 (monosubstitution) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 399 (43) [M]$^{+\cdot}$, 144 (100) [$C_7H_{14}NO_2$]$^+$. $C_{24}H_{33}NO_4$ (399.24): calcd. C 72.15, H 8.33, N 3.51; found C 72.15, H 8.33, N 3.49.

***tert*-Butyl-*N*-6-(4-hydroxyphenyloxy)hexylcarbamate (17):** Hydrogen was bubbled through a suspension of palladium on charcoal (10%, 150 mg) in acid-free chloroform (6 mL) and ethyl acetate (6 mL) for 30 min. Then a solution of compound **16** (595 mg, 1.49 mmol) in a mixture of acid-free chloroform (6 mL) and ethyl acetate (6 mL) was added, and the reaction mixture was flushed 1 h with hydrogen and afterwards it was stirred for 22 h under hydrogen. The solvent was removed under reduced pressure and the residue was purified by filtration through a short column of basic aluminum oxide with chloroform. After removal of the solvent under reduced pressure, product **17** was obtained as a colorless oil (462 mg, 100%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.76 (m_c, 4 H, Ar-2,3,5,6-H), 5.90 (s, 1 H, O*H*), 4.59 (br. s, 1 H, N*H*), 3.86 (t, ^3J = 6.5 Hz, 2 H, OCH_2), 3.15–3.07 (m, 2 H, NHCH_2), 1.72 (quint, ^3J = 7.0 Hz, 2 H, OCH$_2$CH_2), 1.53–1.39 [m, 4 H, NHCH$_2$CH_2, O(CH$_2$)$_2$CH_2], 1.45 (s, 9 H, CH_3), 1.38–1.30 [m, 2 H, NH(CH$_2$)$_2$-CH_2] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.2 (s, *C*ONH), 152.9 (s, Ar-*C*-1), 149.9 (s, Ar-*C*-4), 116.0 (d, Ar-*C*-3,5), 115.6 (d, Ar-*C*-2,6), 79.4 [s, *C*(CH$_3$)$_3$], 68.5 (t, O*C*H$_2$), 40.6 (t, NH*C*H$_2$), 30.0 (t, NHCH$_2$*C*H$_2$), 29.3 (t, OCH$_2$*C*H$_2$), 28.4 (q, *C*H$_3$), 26.5 [t, NH(CH$_2$)$_2$*C*H$_2$], 25.7 [t, O(CH$_2$)$_2$*C*H$_2$] ppm. IR (ATR): $\tilde{\nu}$ = 3341 (O–H), 2933, 2861 (aliph. C–H), 1678 (C=O), 1508 (C=C), 1221, 1164 (C–O), 825 (1,4-disubstitution) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 309 (3) [M]$^{+\cdot}$, 253 (36) [M – C_4H_8]$^{+\cdot}$, 110 (100) [$C_6H_6O_2$]$^{+\cdot}$. MS (CI, isobutane): *m*/*z* (%) = 310 (18) [M + H]$^+$, 254 (100) [M – C_4H_7]$^+$. $C_{17}H_{27}NO_4$ (309.19): calcd. C 65.99, H 8.80, N 4.53; found C 66.13, H 9.02, N 4.56.

***tert*-Butyl-*N*-6-[4-(pent-4-ynyloxy)phenyloxy]hexylcarbamate (18):** A suspension of sodium hydride (217 mg, 5.43 mmol) in anhydrous DMF (20 mL) was cooled to 0 °C, a solution of phenol **17** in anhydrous DMF (15 mL) was added and the mixture was stirred for 15 min at 0 °C. 5-Chloropentyne (352 mg, 3.45 mmol) in anhydrous DMF (5 mL) was added and the reaction mixture was stirred for 22 h at room temperature. Water (70 mL) was added and the solution was extracted with diethyl ether (5× 50 mL). The combined organic layer was dried with magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, dichloromethane, R_f = 0.35) to give **18** as a white solid (891 mg, 78%); m.p. 59 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.82 (m_c, 4 H, Ar-2,3,5,6-H), 4.51 (br. s, 1 H, N*H*), 4.01 [t, ^3J = 6.1 Hz, 2 H, OCH_2(CH$_2$)$_2$C≡CH], 3.89 [t, ^3J = 6.5 Hz, 2 H, OCH_2(CH$_2$)$_5$NH], 3.11 [m_c, 2 H, O(CH$_2$)$_5$CH_2NH], 2.39 [td, ^3J_t = 7.1, ^4J_d = 2.7 Hz, 2 H, O(CH$_2$)$_2$CH_2C≡CH], 2.01–1.94 (m, 3 H, OCH$_2$CH_2CH$_2$C≡C*H*), 1.75 [m_c, 2 H, OCH$_2$CH_2-(CH$_2$)$_4$NH], 1.53–1.42 [m, 4 H, O(CH$_2$)$_2$CH_2CH$_2$CH_2CH$_2$NH], 1.44 (s, 9 H, CH_3), 1.41–1.34 [m, 2 H, O(CH$_2$)$_3$CH_2(CH$_2$)$_2$-NH] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.0 (s, *C*ONH), 153.3 (s, Ar-*C*-1), 153.0 (s, Ar-*C*-4), 115.5, 115.4 (2d, Ar-*C*-2,3,5,6), 83.6 (s, *C*≡CH), 79.0 [s, *C*(CH$_3$)$_3$], 68.7 (d, C≡*C*H), 68.5 [t, O*C*H$_2$(CH$_2$)$_5$NH], 66.8 [t, O*C*H$_2$(CH$_2$)$_2$C≡CH], 40.5 [t, O(CH$_2$)$_5$-*C*H$_2$NH], 30.0 [t, O(CH$_2$)$_4$*C*H$_2$CH$_2$NH], 29.3 [t, OCH$_2$*C*H$_2$(CH$_2$)$_4$-NH], 28.4 (q, *C*H$_3$), 28.3 (t, OCH$_2$*C*H$_2$CH$_2$C≡CH), 26.6 [t, O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$NH], 25.8 [t, O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$NH], 15.2 [t, O(CH$_2$)$_2$*C*H$_2$C≡CH] ppm. IR (ATR): $\tilde{\nu}$ = 3390 (N–H), 3307 (C≡C–H), 2937, 2852 (aliph. C–H), 1689 (C=O), 1511 (C=C), 1234, 1161 (C–O), 816 (1,4-disubstitution) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 375 (64) [M]$^{+\cdot}$, 302 (10) [M – C_4H_9O]$^+$, 176 (89) [$C_6H_{12}O$]$^{+\cdot}$, 110 (100) [$C_6H_6O_2$]$^{+\cdot}$. MS (CI, isobutane): *m*/*z* (%) = 376 (5) [M + H]$^+$, 320 (100) [M – C_4H_7]$^+$, 302 (34) [M – C_4H_9O]$^+$. $C_{22}H_{33}NO_4$ (375.24): calcd. C 70.37, H 8.86, N 3.73; found C 70.08, H 8.90, N 3.72.

6-[4-(Pent-4-ynyloxy)phenyloxy]hexylamine (19): Carbamate **18** (856 mg, 2.28 mmol) was dissolved in dichloromethane (7 mL) and a solution of trifluoroacetic acid (6.50 mL) in dichloromethane (7 mL) was added. The mixture was stirred for 21 h at room temperature and washed with sodium hydroxide solution (1 M, 2× 50 mL) afterwards. The aqueous layer was extracted with dichloromethane (30 mL) and the combined organic layer was washed with brine (40 mL) and dried with magnesium sulfate. The solvent was removed under reduced pressure and the product was obtained as a slightly yellow solid (574 mg, 92%); m.p. 91 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.81 (m_c, 4 H, Ar-2,3,5,6-H), 4.00 [t, ^3J = 6.1 Hz, 2 H, OCH_2(CH$_2$)$_2$C≡CH], 3.89 [t, ^3J = 6.5 Hz, 2 H, OCH_2(CH$_2$)$_5$NH$_2$], 2.72 [m_c, 2 H, O(CH$_2$)$_5$ CH_2NH$_2$], 2.54 (br. s, 2 H, NH_2), 2.39 [td, ^3J_t = 7.1, ^4J_d = 2.6 Hz, 2 H, O(CH$_2$)$_2$-CH_2C≡CH], 2.00–1.93 (m, 3 H, OCH$_2$CH_2CH$_2$C≡C*H*), 1.75 [m_c, 2 H, OCH$_2$CH_2(CH$_2$)$_4$NH$_2$], 1.54–1.43 [m, 4 H, O(CH$_2$)$_2$-CH_2CH$_2$CH_2CH$_2$NH$_2$], 1.42–1.34 [m, 2 H, O(CH$_2$)$_3$CH_2(CH$_2$)$_2$-NH$_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.3 (s, Ar-*C*-1), 153.0 (s, Ar-*C*-4), 115.5, 115.4 (2d, Ar-*C*-2,3,5,6), 83.6 (s, *C*≡CH), 68.8 (d, C≡*C*H), 68.5 [t, O*C*H$_2$(CH$_2$)$_5$NH$_2$], 66.8 [t, O*C*H$_2$(CH$_2$)$_2$-C≡CH], 41.8 [t, O(CH$_2$)$_5$*C*H$_2$NH$_2$], 33.0 [t, O(CH$_2$)$_4$*C*H$_2$-CH$_2$NH$_2$], 29.3 [t, OCH$_2$*C*H$_2$(CH$_2$)$_4$NH$_2$], 28.3 (t, OCH$_2$*C*H$_2$CH$_2$C≡CH), 26.6 [t, O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$NH$_2$], 25.9 [t, O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$NH$_2$], 15.2 [t, O(CH$_2$)$_2$*C*H$_2$C≡CH] ppm. IR (ATR): $\tilde{\nu}$ = 3283 (C≡C–H), 2931, 2861 (aliph. C–H), 1567 (NH$_2$), 1507 (C=C), 1224 (C–O), 826 (1,4-disubstitution) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 275 (16) [M]$^{+\cdot}$, 100 (100) [$C_6H_{14}N$]$^+$. MS (CI, isobutane): *m*/*z* (%) = 276 (100) [M + H]$^+$.

2-Chloro-*N*-{6-[4-(pent-4-ynyloxy)phenyloxy]hexyl}acetamide (20): A solution of chloroacetyl chloride (67.0 μL, 839 μmol) and anhydrous triethylamine (69.3 μL, 500 μmol) in anhydrous dichloromethane (4 mL) was cooled to –10 °C, and amine **19** (135 mg, 490 μmol) in anhydrous dichloromethane (10 mL) was added. The reaction mixture was stirred for 2.5 h at –10 °C and was afterwards filtered with dichloromethane through Celite. The filtrate was washed with brine (2× 30 mL) and the combined organic layer was dried with magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 2:1, R_f = 0.21) to give **20** as a brownish solid (113 mg, 66%); m.p. 60 °C. ^{1}H

NMR (500 MHz, $CDCl_3$): δ = 6.82 (m_c, 4 H, Ar-2,3,5,6-H), 6.59 (br. s, 1 H, N*H*), 4.05 (s, 2 H, ClCH_2), 4.01 [t, ^3J = 6.1 Hz, 2 H, OCH_2(CH$_2$)$_2$C≡CH], 3.90 [t, ^3J = 6.4 Hz, 2 H, NH(CH$_2$)$_5$CH_2O], 3.32 [m_c, 2 H, NHCH_2(CH$_2$)$_5$O], 2.40 [td, ^3J_t = 7.01, ^4J_d = 2.7 Hz, 2 H, O(CH$_2$)$_2$CH_2C≡CH], 2.01–1.94 (m, 3 H, OCH$_2$CH_2CH$_2$-C≡C*H*), 1.77 [m_c, 2 H, NH(CH$_2$)$_4$CH_2CH$_2$O], 1.63–1.55 [m, 2 H, NHCH$_2$CH_2(CH$_2$)$_4$O], 1.54–1.45 [m, 2 H, NH(CH$_2$)$_3$CH_2(CH$_2$)$_2$-O], 1.45–1.38 [m, 2 H, NH(CH$_2$)$_2$CH_2(CH$_2$)$_3$O] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.9 (s, *C*ONH), 153.3 (s, Ar-*C*-1), 153.0 (s, Ar-*C*-4), 115.5, 115.4 (2d, Ar-*C*-2,3,5,6), 83.6 (s, *C*≡CH), 68.8 (d, C≡*C*H), 68.4 [t, NH(CH$_2$)$_5$CH$_2$O], 66.8 [t, OCH$_2$(CH$_2$)$_2$-C≡CH], 42.7 (t, Cl*C*H$_2$), 39.8 [t, NH*C*H$_2$(CH$_2$)$_5$O], 29.3, 29.2 [2t, NHCH$_2$*C*H$_2$(CH$_2$)$_2$*C*H$_2$CH$_2$O], 28.3 (t, OCH$_2$*C*H$_2$CH$_2$C≡CH), 26.6 [t, NH(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$O], 25.8 [t, NH(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$O], 15.2 [t, O(CH$_2$)$_2$*C*H$_2$C≡CH] ppm. IR (ATR): $\tilde{\nu}$ = 3333 (N–H), 3300 (C≡C–H), 2857 (aliph. C–H), 1742 (C=O), 1642, 1510 (arom.), 1232 (C–O), 817 (1,4-disubstitution), 636 (C–Cl) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 351 (49) [M]$^{+\cdot}$, 176 (76) [$C_{11}H_{12}O_2$]$^+$, 110 (100) [$C_6H_6O_2$]$^+$. MS (CI, isobutane): *m*/*z* (%) = 352 (60) [M + H]$^+$, 189 (100) [$C_{12}H_{13}O_2$]$^{+\cdot}$. $C_{19}H_{26}ClNO_3$ (351.87): calcd. C 64.85, H 7.45, N 3.98; found C 64.80, H 7.44, N 4.01.

1-(2-Oxo-2-{6-[4-(pent-4-ynyloxy)phenyloxy]hexylamino}ethyl)-3-{4-[tris(4-*tert*-butylphenyl)methyl]phenyl}pyridinium Iodide (21): A mixture of stopper **11** (71.1 mg, 126 μmol), alkyne linker **20** (50.0 mg, 142 μmol) and sodium iodide (28.4 mg, 189 μmol) in 1,4-dioxane (12 mL) was heated at reflux for 17 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, dichloromethane/methanol, 10:1, R_f = 0.40) to give **21** as a yellow solid (65.1 mg, 51%); m.p. 218 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.37 (s, 1 H, Py-2-H), 9.07 (d, ^3J = 6.1 Hz, 1 H, Py-6-H), 8.53 (t, ^3J = 5.6 Hz, 1 H, CON*H*), 8.49 (d, ^3J = 8.4 Hz, 1 H, Py-4-H), 7.95 (dd, ^3J = 8.2, ^3J = 6.1 Hz, 1 H, Py-5-H), 7.60 (d, ^3J = 8.7 Hz, 2 H, PyAr-2,6-H), 7.43 (d, ^3J = 8.7 Hz, 2 H, PyAr-3,5-H), 7.26 (d, ^3J = 8.7 Hz, 6 H, *t*BuAr-3,5-H), 7.10 (d, ^3J = 8.7 Hz, 6 H, *t*BuAr-2,6-H), 6.80 (m_c, 4 H, OAr-2,3,5,6-H), 5.96 (s, 2 H, PyCH_2), 3.99 [t, ^3J = 6.1 Hz, 2 H, OCH_2(CH$_2$)$_2$C≡CH], 3.86 [t, ^3J = 6.5 Hz, 2 H, OCH_2(CH$_2$)$_5$-NH], 3.28 [m_c, 2 H, O(CH$_2$)$_5$CH_2NH], 2.38 [td, ^3J_t = 7.0, ^4J_d = 2.7 Hz, 2 H, O(CH$_2$)$_2$CH_2C≡CH], 1.99–1.93 (m, 3 H, OCH$_2$CH_2CH$_2$C≡C*H*), 1.79–1.60 [m, 4 H, OCH$_2$CH_2(CH$_2$)$_2$-CH_2CH$_2$NH], 1.49–1.38 [m, 4 H, O(CH$_2$)$_2$CH_2CH_2(CH$_2$)$_2$NH], 1.31 [s, 27 H, C(CH_3)$_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.0 (s, *C*ONH), 153.3 (s, OAr-*C*-1), 152.9 (s, OAr-*C*-4), 151.2 (s, PyAr-*C*-4), 148.8 (s, *t*BuAr-*C*-4), 143.2 (d, Py-*C*-2), 143.1 (s, *t*BuAr-*C*-1), 142.8 (d, Py-*C*-6), 142.4 (d, Py-*C*-4), 141.4 (s, Py-*C*-3), 132.7 (d, PyAr-*C*-3,5), 130.6 (d, *t*BuAr-*C*-2,6), 129.4 (s, PyAr-*C*-1), 127.5 (d, Py-*C*-5), 126.3 (d, PyAr-*C*-2,6), 124.4 (d, *t*BuAr-*C*-3,5), 115.5 (d, OAr-*C*-2,3,5,6), 83.6 (s, *C*≡CH), 68.8 (d, C≡*C*H), 68.4 [t, OCH$_2$(CH$_2$)$_5$NH], 66.8 [t, OCH$_2$(CH$_2$)$_2$C≡CH], 63.7 [s, (*t*BuAr)$_3$*C*], 62.5 (t, Py-*C*H$_2$), 40.2 [t, O(CH$_2$)$_5$CH$_2$NH], 34.3 [s, *C*(CH$_3$)$_3$], 31.3 (q, *C*H$_3$), 29.2 [t, OCH$_2$*C*H$_2$(CH$_2$)$_4$NH], 28.8 [t, O(CH$_2$)$_4$*C*H$_2$CH$_2$NH], 28.3 (t, OCH$_2$*C*H$_2$CH$_2$C≡CH), 26.7 [t, O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$NH], 25.6 [t, O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$NH], 15.2 [t, O(CH$_2$)$_2$*C*H$_2$C≡CH] ppm. IR (ATR): $\tilde{\nu}$ = 3278 (N–H), 3226 (C≡C–H), 3046 (arom. C–H), 2953, 2904, 2865 (aliph. C–H), 1683 (C=O), 1506 (C=C), 1224 (C–O), 823 (1,4-disubstitution) cm^{-1}. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 882 [M – I]$^+$. $C_{61}H_{73}IN_2O_3$ (1008.47): C 72.60, H 7.29, N 2.78. $C_{61}H_{73}IN_2O_3 \cdot 1.5H_2O$ (1035.48): calcd. C 70.71, H 7.39, N 2.70; found C 70.64, H 7.25, N 2.84.

1-(2-Oxo-2-{6-[4-(pent-4-ynyloxy)phenyloxy]hexylamino}ethyl)-3-{4-[tris(4-*tert*-butylphenyl)methyl]phenyl}pyridinium Hexafluorophosphate (22): To a solution of iodide **21** (166 mg, 165 μmol) in anhydrous dichloromethane (5 mL), a solution of silver(I) hexafluorophosphate (44.0 mg, 174 μmol) in anhydrous dichloromethane (2 mL) was added. The reaction mixture was stirred for 1 h at room temperature and then filtered. The filtrate was concentrated under reduced pressure and purified two times by column chromatography (silica gel, 1. dichloromethane/methanol, 10:1, R_f = 0.43; 2. dichloromethane/methanol, 40:1, R_f = 0.13) to give **22** as a orange solid (122 mg, 72%); m.p. 156 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.81 (br. s, 1 H, Py-2-H), 8.61 (d, ^3J = 5.9 Hz, 1 H, Py-6-H), 8.45 (d, ^3J = 8.2 Hz, 1 H, Py-4-H), 7.92 (dd, ^3J = 8.0, ^3J = 6.1 Hz, 1 H, Py-5-H), 7.47 (d, ^3J = 8.5 Hz, 2 H, PyAr-2,6-H), 7.41 (d, ^3J = 8.5 Hz, 2 H, PyAr-3,5-H), 7.26 (d, ^3J = 5.6 Hz, 6 H, *t*BuAr-3,5-H), 7.15 (br. s, 1 H, N*H*), 7.10 (d, ^3J = 5.6 Hz, 6 H, *t*BuAr-2,6-H), 6.79 (m_c, 4 H, OAr-2,3,5,6-H), 5.38 (s, 2 H, PyCH_2), 3.99 [t, ^3J = 6.1 Hz, 2 H, OCH_2(CH$_2$)$_2$C≡CH], 3.86 [t, ^3J = 6.5 Hz, 2 H, OCH_2(CH$_2$)$_5$NH], 3.27 [m_c, 2 H, O(CH$_2$)$_5$CH_2NH], 2.38 [m_c, 2 H, O(CH$_2$)$_2$CH_2C≡CH], 1.99–1.93 (m, 3 H, OCH$_2$CH_2CH$_2$C≡C*H*), 1.75–1.69 [m, 2 H, OCH$_2$CH_2(CH$_2$)$_4$NH], 1.61–1.54 [m, 2 H, O(CH$_2$)$_4$CH_2CH$_2$NH], 1.48–1.34 [m, 4 H, O(CH$_2$)$_2$CH_2CH_2(CH$_2$)$_2$NH], 1.30 [s, 27 H, C(CH_3)$_3$] ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.0 (s, *C*ONH), 153.3 (s, OAr-*C*-1), 152.9 (s, OAr-*C*-4), 151.0 (s, PyAr-*C*-4), 148.8 (s, *t*BuAr-*C*-4), 143.3 (d, Py-*C*-2), 143.1 (s, *t*BuAr-*C*-1), 143.0 (d, Py-*C*-6), 142.8 (d, Py-*C*-4), 141.5 (s, Py-*C*-3), 132.7 (d, PyAr-*C*-3,5), 130.6 (d, *t*BuAr-*C*-2,6), 129.6 (s, PyAr-*C*-1), 127.6 (d, Py-*C*-5), 126.2 (d, PyAr-*C*-2,6), 124.4 (d, *t*BuAr-*C*-3,5), 115.5, 115.4 (2d, OAr-*C*-2,3,5,6), 83.6 (s, *C*≡CH), 68.8 (d, C≡*C*H), 68.4 [t, OCH$_2$(CH$_2$)$_5$-NH], 66.8 [t, OCH$_2$(CH$_2$)$_2$C≡CH], 63.7 [s, (*t*BuAr)$_3$*C*], 62.5 (t, Py-*C*H$_2$), 40.4 [t, O(CH$_2$)$_5$CH$_2$NH], 34.3 [s, *C*(CH$_3$)$_3$], 31.4 (q, *C*H$_3$), 29.1 [t, OCH$_2$*C*H$_2$(CH$_2$)$_4$NH], 28.8 [t, O(CH$_2$)$_4$*C*H$_2$CH$_2$NH], 28.3 (t, OCH$_2$*C*H$_2$CH$_2$C≡CH), 26.5 [t, O(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$NH], 25.6 [t, O(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_3$NH], 15.1 [t, O(CH$_2$)$_2$*C*H$_2$C≡CH] ppm. IR (ATR): $\tilde{\nu}$ = 3417 (N–H), 3292 (C≡C–H), 3091, 3043 (arom. C–H), 2955, 2904, 2866 (aliph. C–H), 1684 (C=O), 1506 (C=C), 1227 (C–O), 824 (1,4-disubstitution) cm^{-1}. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 882 [M – PF_6]$^+$. $C_{61}H_{73}F_6N_2O_3P$ (1026.53): C 71.32, H 7.16, N 2.73. $C_{61}H_{73}F_6N_2O_3P \cdot 3H_2O$ (1080.56): calcd. C 67.76, H 7.36, N 2.59; found C 67.53, H 7.26, N 2.67.

[2]-{[(1-{2-Oxo-2-[(6-{4-[3-(1-{6-[3,3,3-tris(4-*tert*-butylphenyl)propyloxy]-6-oxohexyl}-1,2,3-triazol-4-yl)propyloxy]}phenyloxy)hexyl]-amino}ethyl)-3-{4-[tris(4-*tert*-butylphenyl)methyl]phenyl}pyridinium-hexafluorophosphat]-*rotaxa*-[5^4-methoxy-3,7,10,21-tetraoxa-1,9(1,4)-dibenzena-5(2,6)-pyridina-heneicosaphan]} (23): Macrocycle **2** (27.0 mg, 52.0 μmol), alkyne half-axis **22** (53.4 mg, 52.0 μmol) and azide half-axis **7** (32.2 mg, 54.1 μmol) were dissolved in anhydrous dichloromethane (5 mL), and copper(I) tetrakisacetonitrilo hexafluorophosphate (20.0 mg, 53.7 μmol) was added. The reaction mixture was stirred at room temperature for 2 d and afterwards it was diluted with dichloromethane (3 mL) and methanol (5 mL). A solution of potassium cyanide (20.0 mg, 307 μmol) in methanol (5 mL) was added and the mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and dichloromethane (15 mL) was added. The organic layer was washed with water (15 mL) and the aqueous layer was extracted with dichloromethane (2 × 5 mL). The combined organic layer was dried with magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified two times by column chromatography (silica gel, dichloromethane/methanol, 40:1, R_f = 0.35) to afford rotaxane **23** (3.0 mg, 3%) and axis **24** (27 mg, 32%) as yellow solids.

Rotaxane 23: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.72 (s, 1 H, Py^1-2-H), 7.89 (d, ^3J = 7.8 Hz, 1 H, Py^1-4-H), 7.81 (d, ^3J = 6.0 Hz, 1 H, Py^1-6-H), 7.49 (m_c, 1 H, Py^1-5-H), 7.34–7.28 (m, 7 H, Ar^1-3,5-

H, triazol-5-H), 7.28–7.23 (m, 6 H, Ar[4]-3,5-H), 7.21–7.15 (m, 12 H, Ar[1]-2,6-H, Ar[4]-2,6-H), 7.13 (d, ^3J = 8.2 Hz, 2 H, Ar[2]-2,6-H), 7.10 (d, ^3J = 8.2 Hz, 2 H, Ar[2]-3,5-H), 6.98 (m_c, 1 H, N*H*), 6.85 (d, ^3J = 8.2 Hz, 4 H, Ar[5]-2,6-H), 6.83–6.79 (m, 6 H, Ar[3]-2,3,5,6-H, Py[2]-3,5-H), 6.30 (d, ^3J = 8.5 Hz, 4 H, Ar[5]-3,5-H), 5.00 (s, 2 H, Py[1]C*H*$_2$), 4.46–4.26 [m, 10 H, Py[2]C*H*$_2$OC*H*$_2$Ar[5], triazol-C*H*$_2$-(CH$_2$)$_4$COO], 3.98–3.85 (m, 6 H, C*H*$_2$OAr[3]OC*H*$_2$, COOC*H*$_2$CH$_2$), 3.83 (s, 3 H, Py[2]-OC*H*$_3$), 3.72–3.66 (m, 4 H, Ar[5]OC*H*$_2$), 3.07 (m_c, 2 H, NHC*H*$_2$), 2.92–2.86 [m, 4 H, Ar[3]O(CH$_2$)$_2$C*H*$_2$-triazol, COOCH$_2$C*H*$_2$], 2.22 [t, ^3J = 7.4 Hz, 2 H, triazol-(CH$_2$)$_4$C*H*$_2$COO], 2.13 (m_c, 2 H, Ar[3]OCH$_2$C*H*$_2$CH$_2$-triazol), 1.92–1.84 [m, 2 H, triazol-CH$_2$C*H*$_2$(CH$_2$)$_3$COO], 1.71 [m_c, 2 H, NH(CH$_2$)$_4$C*H*$_2$CH$_2$-OAr[3]], 1.68–1.54 [m, 8 H, NHCH$_2$C*H*$_2$, triazol-(CH$_2$)$_3$C*H*$_2$CH$_2$-COO, Ar[5]OCH$_2$C*H*$_2$], 1.46–1.23 [m, 18 H, NH(CH$_2$)$_2$C*H*$_2$C*H*$_2$, triazol-(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_2$COO, Ar[5]O(CH$_2$)$_2$C*H*$_2$C*H*$_2$C*H*$_2$], 1.31, 1.29 [2s, 54 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ = 173.4 (s, *C*OOCH$_2$), 167.1 (s, Py[2]-*C*-4), 163.0 (s, *C*ONH), 158.9 (s, Py[2]-*C*-2,6), 158.4 (s, Ar[5]-*C*-4), 153.3 (s, Ar[3]-*C*-1), 153.0 (s, Ar[3]-*C*-4), 150.5 (s, Ar[2]-*C*-4), 148.7 (s, Ar[1]-*C*-4), 148.5 (s, Ar[4]-*C*-4), 147.4 (s, triazol-*C*-4), 145.1 (d, Py[1]-*C*-2), 143.8 (s, Ar[4]-*C*-1), 143.4 (s, Ar[1]-*C*-1), 142.0 (d, Py[1]-*C*-6), 140.7 (d, Py[1]-*C*-4), 139.8 (s, Py[1]-*C*-3), 130.6 (d, Ar[2]-*C*-3,5), 130.5 (d, Ar[1]-*C*-2,6), 130.1 (d, Ar[5]-*C*-2,6), 129.4 (s, Ar[2]-*C*-1), 129.1 (s, Ar[5]-*C*-1), 128.5 (d, Ar[4]-*C*-2,6), 126.2 (d, Ar[2]-*C*-2,6), 125.8 (d, Py[1]-*C*-5), 124.7 (d, Ar[4]-*C*-3,5), 124.5 (d, Ar[1]-*C*-3,5), 120.8 (d, triazol-*C*-5), 115.4 (d, Ar[3]-*C*-2,3,5,6), 113.9 (d, Ar[5]-*C*-3,5), 107.6 (d, Py[2]-*C*-3,5), 73.0 (t, Py[2]CH$_2$OCH$_2$Ar[5]), 72.3 (t, Py[2]*C*H$_2$OCH$_2$Ar[5]), 68.4 [t, OCH$_2$(CH$_2$)$_5$NH], 67.5 [t, OCH$_2$(CH$_2$)$_2$triazol], 67.1 (t, Ar[5]OCH$_2$), 63.8 [s, *C*(Ar[1])$_3$Ar[2]], 63.0 (t, COOCH$_2$CH$_2$), 61.7 (t, PyCH$_2$CONH), 55.4 (q, OCH$_3$), 53.7 [s, *C*(Ar[4])$_3$], 49.9 [t, triazol-*C*H$_2$(CH$_2$)$_4$COO], 40.1 [t, NHCH$_2$(CH$_2$)$_5$-OAr[3]], 38.7 (t, COOCH$_2$CH$_2$), 34.4, 34.3 [2s, *C*(CH$_3$)$_3$], 33.9 [t, triazol-(CH$_2$)$_4$CH$_2$COO], 31.4 [q, C(*C*H$_3$)$_3$], 30.1 [t, triazol-CH$_2$*C*H$_2$(CH$_2$)$_3$COO], 29.3 [t, Ar[5]O(CH$_2$)$_4$*C*H$_2$][#]*, 29.2 [t, NH(CH$_2$)$_4$*C*H$_2$CH$_2$OAr[3]], 29.1 (t, Ar[3]OCH$_2$*C*H$_2$CH$_2$triazol), 28.8 (t, NHCH$_2$*C*H$_2$), 28.6 {t, Ar[5]OCH$_2$*C*H$_2$, [Ar[5]O(CH$_2$)$_3$*C*H$_2$][#]}*, 26.6 [t, NH(CH$_2$)$_2$*C*H$_2$]*, 26.3 [t, triazol-(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_2$COO]*, 25.9 [t, Ar[5]O(CH$_2$)$_2$*C*H$_2$]*, 25.7 [t, NH(CH$_2$)$_3$*C*H$_2$]*, 24.3 (t, *C*H$_2$CH$_2$COO)*, 22.2 [t, Ar[3]O(CH$_2$)$_2$*C*H$_2$triazol] ppm. *The signals were assigned by comparison with free axis **24** and free macrocycle **2**. [#]The assignment may be inverted. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 1997 [M – PF$_6$]$^+$.

Axis 24: ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.89 (s, 1 H, Py[1]-2-H), 8.65 (d, ^3J = 6.1 Hz, 1 H, Py[1]-6-H), 8.48 (d, ^3J = 8.4 Hz, 1 H, Py[1]-4-H), 7.93 (m_c, 1 H, Py[1]-5-H), 7.48 (d, ^3J = 8.6 Hz, 2 H, Ar[2]-2,6-H), 7.45 (br. s, 1 H, CON*H*), 7.42 (d, ^3J = 8.6 Hz, 2 H, Ar[2]-3,5-H), 7.28–7.23 (m, 13 H, Ar[1]-3,5-H, Ar[4]-3,5-H, triazol-5-H), 7.17 (d, ^3J = 8.6 Hz, 6 H, Ar[4]-2,6-H), 7.10 (d, ^3J = 8.6 Hz, 6 H, Ar[1]-2,6-H), 6.78 (s, 4 H, Ar[3]-2,3,5,6-H), 5.42 (s, 2 H, Py[1]C*H*$_2$), 4.29 [t, ^3J = 7.2 Hz, 2 H, triazol-C*H*$_2$(CH$_2$)$_4$COO], 3.92 [t, 2 H, Ar[3]OC*H*$_2$(CH$_2$)$_2$triazol], 3.90–3.88 (m, 2 H, COOC*H*$_2$CH$_2$), 3.86 [t, ^3J = 6.4 Hz, 2 H, NH(CH$_2$)$_5$C*H*$_2$OAr[3]], 3.27 (m_c, 2 H, NHC*H*$_2$), 2.91–2.85 [m, 4 H, COOCH$_2$C*H*$_2$, Ar[3]O(CH$_2$)$_2$C*H*$_2$triazol], 2.22 [t, ^3J = 7.4 Hz, 2 H, triazol-(CH$_2$)$_4$C*H*$_2$COO], 2.12 (m_c, 2 H, Ar[3]OCH$_2$C*H*$_2$CH$_2$triazol), 1.88 [quint, 2 H, triazol-CH$_2$C*H*$_2$(CH$_2$)$_3$-COO], 1.72 [m_c, 2 H, NH(CH$_2$)$_4$C*H*$_2$CH$_2$OAr[3]], 1.66–1.54 [m, 4 H, NHCH$_2$C*H*$_2$, triazol-(CH$_2$)$_3$C*H*$_2$CH$_2$COO], 1.49–1.32 [m, 6 H, NH(CH$_2$)$_2$C*H*$_2$C*H*$_2$(CH$_2$)$_2$OAr[3], triazol-(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_2$COO], 1.30, 1.28 [2s, 54 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 173.4 (s, *C*OOCH$_2$), 162.9 (s, *C*ONH), 153.3 (s, Ar[3]-*C*-1), 153.0 (s, Ar[3]-*C*-4), 151.1 (s, Ar[2]-*C*-4), 148.8 (s, Ar[1]-*C*-4), 148.5 (s, Ar[4]-*C*-4), 147.3 (s, triazol-*C*-4)*, 143.8 (s, Ar[4]-*C*-1), 143.3 (d, Py[1]-*C*-2), 143.1 (s, Ar[1]-*C*-1), 142.9 (d, Py[1]-*C*-6), 142.7 (d, Py[1]-*C*-4), 141.6 (s, Py[1]-*C*-3), 132.7 (d, Ar[2]-*C*-3,5), 130.6 (d, Ar[1]-*C*-2,6), 129.6 (s, Ar[2]-*C*-1), 128.5 (d, Ar[4]-*C*-2,6), 127.6 (d, Py[1]-*C*-5), 126.2 (d, Ar[2]-*C*-2,6), 124.7 (d, Ar[4]-*C*-3,5), 124.4 (d, Ar[1]-*C*-3,5), 120.8 (d, triazol-*C*-5), 115.4, 115.4 (2d, Ar[3]-*C*-2,3,5,6), 68.4 [t, NH(CH$_2$)$_5$*C*H$_2$OAr[3]], 67.4 [t, Ar[3]O*C*H$_2$(CH$_2$)$_2$triazol], 63.7 [s, *C*(Ar[1])$_3$Ar[2]], 62.9 (t, COO*C*H$_2$-CH$_2$), 62.6 (t, Py[1]*C*H$_2$), 53.7 [s, *C*(Ar[4])$_3$], 49.9 [t, triazol-*C*H$_2$(CH$_2$)$_4$-COO], 40.4 (t, NH*C*H$_2$), 38.7 (t, COO*C*H$_2$CH$_2$), 34.3, 34.3 [2s, *C*(CH$_3$)$_3$], 33.9 [t, triazol-(CH$_2$)$_4$*C*H$_2$COO], 31.3 [q, C(*C*H$_3$)$_3$], 30.0 [t, triazol-CH$_2$*C*H$_2$(CH$_2$)$_3$COO], 29.1, 29.1 (2 t, *C*H$_2$CH$_2$-OAr[3]OCH$_2$*C*H$_2$), 28.8 (t, NHCH$_2$*C*H$_2$), 26.4 [t, NH(CH$_2$)$_2$*C*H$_2$], 26.0 [t, triazol-(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_2$COO], 25.6 [t, NH(CH$_2$)$_3$*C*H$_2$], 24.2 [t, triazol-(CH$_2$)$_3$*C*H$_2$CH$_2$COO], 22.2 [t, Ar[3]O(CH$_2$)$_2$*C*H$_2$-triazol] ppm. * The signal was only observed in the HMBC spectrum. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 1477 [M – PF$_6$]$^+$.

***tert*-Butyl-*N*-6-(4-{6-[4-(benzyloxy)phenyloxy]hexyloxy}phenyloxy)-hexylcarbamate (25):** A suspension of sodium hydride (249 mg, 8.73 mmol) in anhydrous DMF (20 mL) was cooled to 0 °C, and phenol **17** (1.57 g, 5.08 mmol) in anhydrous DMF (20 mL) was added. The reaction mixture was stirred for 15 min at 0 °C and bromide **13** (2.05 g, 5.66 mmol) in anhydrous DMF (25 mL) was added. The solution was stirred at room temperature for 2 d and afterwards water (50 mL) was added. The aqueous layer was extracted with dichloromethane (3 × 100 mL), the combined organic layer was washed with brine (100 mL) and dried with magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by crystallization from *n*-hexane/dichloromethane to give **25** as a white solid (2.25 g, 75%); m.p. 117 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.42–7.40 (m, 2 H, Bn-2,6-H), 7.37 (m_c, 2 H, Bn-3,5-H), 7.32–7.29 (m, 1 H, Bn-4-H), 6.90 (d, ^3J = 9.1 Hz, 2 H, Ar[2]-3,5-H), 6.84–6. 79 (m, 6 H, Ar[2]-2,6-H, Ar[1]-2,3,5,6-H), 5.00 (s, 2 H, BnC*H*$_2$), 4.50 (br. s, 1 H, N*H*), 3.91 (t, ^3J = 6.5 Hz, 2 H, OC*H*$_2$)*, 3.90 (t, ^3J = 6.5 Hz, 2 H, OC*H*$_2$)*, 3.89 (t, ^3J = 6.5 Hz, 2 H, OC*H*$_2$)*, 3.11 (m_c, 2 H, NHC*H*$_2$), 1.85–1.70 (m, 6 H, OCH$_2$C*H*$_2$), 1.55–1.46 [m, 8 H, NHCH$_2$C*H*$_2$, O(CH$_2$)$_2$-C*H*$_2$], 1.44 (s, 9 H, C*H*$_3$), 1.41–1.35 [m, 2 H, NH(CH$_2$)$_2$C*H*$_2$] ppm. *An exact assignment was not possible. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 156.0 (s, *C*ONH), 153.5, 153.2 (2s, Ar[1]-*C*-1,4, Ar[2]-*C*-1), 152.9 (s, Ar[2]-*C*-4), 137.4 (s, Bn-*C*-1), 128.5 (d, Bn-*C*-3,5), 127.8 (d, Bn-*C*-4), 127.5 (d, Bn-*C*-2,6), 115.8 (d, Ar[2]-*C*-3,5), 115.4 (d, Ar[2]-*C*-2,6, Ar[1]-*C*-2,3,5,6), 79.0 [s, *C*(CH$_3$)$_3$], 70.7 (t, Bn*C*H$_2$), 68.5, 68.4 (2t, O*C*H$_2$), 40.5 (t, NH*C*H$_2$), 30.0 (t, NHCH$_2$*C*H$_2$), 29.3 (t, OCH$_2$*C*H$_2$), 28.4 (q, *C*H$_3$), 26.6 [t, NH(CH$_2$)$_2$*C*H$_2$], 25.9, 25.8 [2t, O(CH$_2$)$_2$*C*H$_2$] ppm. IR (ATR): $\tilde{\nu}$ = 3351 (N–H), 2940, 2866 (aliph. C–H), 1689 (C=O), 1507 (C=C), 1230, 1172, 1026 (C–O), 829 (1,4-disubstitution), 737, 694 (monosubstitution) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 591 (16) [M]$^{+\cdot}$, 517 (100) [M – C$_4$H$_{10}$O]$^{+\cdot}$. MS (CI, isobutane): *m*/*z* (%) = 518 (34) [M – C$_4$H$_9$O]$^+$, 113 (100). C$_{36}$H$_{49}$NO$_6$ (591.36): calcd. C 73.07, H 8.35, N 2.37; found C 73.29, H 8.37, N 2.36.

***tert*-Butyl-*N*-6-{4-[6-(4-hydroxyphenyloxy)hexyloxy]phenyloxy}-hexylcarbamate (26):** Hydrogen was bubbled through a suspension of palladium on charcoal (10%, 239 mg) in acid-free chloroform (15 mL) for 30 min. A solution of benzyl ether **25** (1.38 g, 2.34 mmol) in acid-free chloroform (40 mL) was added, and the mixture was flushed 1 h with hydrogen. Afterwards the reaction mixture was stirred for 22 h under hydrogen. The solvent was removed under reduced pressure and the residue was filtered with chloroform through a small column of silica gel to yield **26** as a white solid (1.11 g, 94%); m.p. 102 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 6.80 (s, 4 H, Ar[1]-2,3,5,6-H), 6.76 (m_c, 4 H, Ar[2]-2,3,5,6-H), 5.21 (br. s, 1 H, O*H*), 4.54 (br. s, 1 H, N*H*), 3.91 (t, ^3J = 6.5 Hz, 2 H, OC*H*$_2$)*, 3.90 (t, ^3J = 6.5 Hz, 2 H, OC*H*$_2$)*, 3.89 (t, ^3J = 6.5 Hz, 2 H, OC*H*$_2$)*, 3.11 (m_c, 2 H, NHC*H*$_2$), 1.82–1.70 (m, 6 H, OCH$_2$C*H*$_2$), 1.54–1.46 (m, 8 H, NHCH$_2$C*H*$_2$, OCH$_2$CH$_2$C*H*$_2$),

1.45 (s, 9 H, CH_3), 1.40–1.32 [m, 2 H, NH(CH$_2$)$_2$CH_2] ppm. *An exact assignment was not possible. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.1 (s, *C*ONH), 153.2, 153.2, 153.1 (3s, Ar^1-*C*-1,4, Ar^2-*C*-1), 149.7 (s, Ar^2-*C*-4), 116.0, 115.6, 115.5, 115.4 (4d, Ar^1-*C*-2,3,5,6, Ar^2-*C*-2,3,5,6), 79.2 [s, *C*(CH$_3$)$_3$], 68.5, 68.5, 68.5 (3t, O*C*H$_2$), 40.5 (t, NH*C*H$_2$), 30.0 (t, NHCH$_2$*C*H$_2$), 29.3, 29.3 (2t, OCH$_2$*C*H$_2$), 28.4 (q, *C*H$_3$), 26.5 [t, NH(CH$_2$)$_2$*C*H$_2$], 25.8, 25.7 [2t, O(CH$_2$)$_2$-*C*H$_2$] ppm. IR (ATR): $\tilde{\nu}$ = 3430 (N–H), 3299 (O–H), 2940, 2908, 2869 (aliph. C–H), 1660 (C=O), 1510 (C=C), 1472 (C–H), 1363 (O–H), 1235, 1221, 1031 (C–O), 829 (1,4-disubstitution) cm^{-1}. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 524 [M + Na]$^+$, 501 [M]$^{+\cdot}$, 402 [M – C$_5$H$_9$O$_2$ + 2 H]$^+$. $C_{29}H_{43}NO_6$ (501.31): calcd. C 69.43, H 8.64, N 2.79; found C 69.12, H 8.69, N 2.78.

***tert*-Butyl-*N*-6-(4-{6-[4-(pent-4-ynyloxy)phenyloxy]hexyloxy}-phenyloxy)hexylcarbamate (27):** A suspension of sodium hydride (381 mg, 9.53 mmol) in anhydrous DMF (4 mL) was cooled to 0 °C, and phenol **26** (1.06 g, 2.11 mmol) in anhydrous DMF (30 mL) was added. The mixture was stirred for 15 min at 0 °C and 5-chloropentyne (362 mg, 3.55 mmol) was added. The reaction mixture was stirred for 18 h at room temperature and afterwards water (50 mL) was added and the solution was extracted with dichloromethane (5× 70 mL). The combined organic layer was dried with magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, chloroform, R_f = 0.08) to give **27** as a white solid (916 mg, 76%); m.p. 98 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.82 (m$_c$, 4 H, Ar^1-2,3,5,6-H or Ar^2-2,3,5,6-H), 6.81 (s, 4 H, Ar^1-2,3,5,6-H or Ar^2-2,3,5,6-H), 4.50 (br. s, 1 H, N*H*), 4.01 [t, ^3J = 6.2 Hz, 2 H, OCH_2(CH$_2$)$_2$C≡CH], 3.91 (t, ^3J = 6.5 Hz, 2 H, OCH_2)*, 3.91 (t, ^3J = 6.5 Hz, 2 H, OCH_2)*, 3.89 (t, ^3J = 6.5 Hz, 2 H, OCH_2)*, 3.12 (m$_c$, 2 H, NHCH_2), 2.40 [td, ^3J_t = 7.0 Hz, ^4J_d = 2.7 Hz, 2 H, O(CH$_2$)$_2$CH_2C≡CH], 2.00–1.94 (m, 3 H, OCH$_2$CH_2CH$_2$C≡C*H*), 1.83–1.71 (m, 6 H, OCH$_2$CH_2), 1.56–1.46 (m, 8 H, NHCH$_2$CH_2, OCH$_2$CH$_2$CH_2), 1.44 (s, 9 H, CH_3), 1.41–1.33 [m, 2 H, NH(CH$_2$)$_2$CH_2] ppm. *An exact assignment was not possible. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.0 (s, *C*ONH), 153.3, 153.2, 153.1, 153.0 (4s, Ar^1-*C*-1,4, Ar^2-*C*-1,4), 115.5, 115.4, 115.4, 115.4 (4d, Ar^1-*C*-2,3,5,6, Ar^2-*C*-2,3,5,6), 83.6 (s, *C*≡CH), 79.0 [s, *C*(CH$_3$)$_3$], 68.7 (d, C≡*C*H), 68.5, 68.5 (2t, O*C*H$_2$), 66.8 [t, O*C*H$_2$(CH$_2$)$_2$C≡CH], 40.5 (t, NH*C*H$_2$), 30.0 (t, NHCH$_2$*C*H$_2$), 29.3, 29.3 (2t, OCH$_2$*C*H$_2$), 28.4 (q, *C*H$_3$), 28.3 (t, OCH$_2$*C*H$_2$-CH$_2$C≡CH), 26.6 [t, NH(CH$_2$)$_2$*C*H$_2$], 25.9, 25.8 [2t, O(CH$_2$)$_2$*C*H$_2$], 15.2 [t, O(CH$_2$)$_2$*C*H$_2$C≡CH] ppm. IR (ATR): $\tilde{\nu}$ = 3360 (N–H), 3310 (C≡C–H), 2940, 2915, 2867 (aliph. C–H), 1687 (C=O), 1508 (C=C), 1474 (C–H), 1228, 1169, 1027 (C–O), 828 (1,4-disubstitution) cm^{-1}. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 590 [M + Na]$^+$, 567 [M]$^{+\cdot}$. $C_{34}H_{49}NO_6$ (567.36): calcd. C 71.93, H 8.70, N 2.47; found C 71.45, H 8.69, N 2.45.

6-(4-{6-[4-(Pent-4-ynyloxy)phenyloxy]hexyloxy}phenyloxy)hexylamine (28): Carbamate **27** (284 mg, 501 μmol) was dissolved in dichloromethane (6 mL), and trifluoroacetic acid (1.4 mL) in dichloromethane (1 mL) was added. The reaction mixture was stirred for 19 h at room temperature and washed with aqueous sodium hydroxide solution (1 M, 2× 25 mL). The aqueous layer was extracted with dichloromethane (30 mL), the combined organic layer was washed with brine (40 mL) and dried with magnesium sulfate. The solvent was removed under reduced pressure and the product was obtained as a white solid (222 mg, 95%); m.p. 104–106 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.82 (s, 4 H, Ar^1-2,3,5,6-H or Ar^2-2,3,5,6-H), 6.81 (s, 4 H, Ar^1-2,3,5,6-H or Ar^2-2,3,5,6-H), 4.01 [t, ^3J = 6.1 Hz, 2 H, OCH_2(CH$_2$)$_2$C≡CH], 3.93–3.88 (m, 6 H, OCH_2), 2.70 (t, ^3J = 7.0 Hz, 2 H, NH$_2$CH_2), 2.40 [td, ^3J_t = 7.0 Hz, ^4J_d = 2.6 Hz, 2 H, O(CH$_2$)$_2$CH_2C≡CH], 2.01–1.94 (m, 3 H, OCH$_2$CH_2CH$_2$C≡C*H*), 1.82–1.72 (m, 6 H, OCH$_2$CH_2), 1.55–1.50 [m, 4 H, O(CH$_2$)$_2$CH_2], 1.50–1.43 [m, 4 H, NH$_2$CH$_2$CH_2CH$_2$CH_2-(CH$_2$)$_2$O], 1.42–1.35 [m, 2 H, NH(CH$_2$)$_2$CH_2] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.3, 153.2, 153.2, 153.0 (4s, Ar^1-*C*-1,4, Ar^2-*C*-1,4), 115.5, 115.4 (2d, Ar^1-*C*-2,3,5,6, Ar^2-*C*-2,3,5,6), 83.6 (s, *C*≡CH), 68.7 (d, C≡*C*H), 68.5, 68.5 (2t, O*C*H$_2$), 66.8 [t, OCH$_2$(CH$_2$)$_2$C≡CH], 42.2 (t, NH$_2$*C*H$_2$), 33.8 (t, NHCH$_2$*C*H$_2$), 29.4, 29.3 (2t, OCH$_2$*C*H$_2$), 28.3 (t, OCH$_2$*C*H$_2$CH$_2$C≡CH), 26.7 [t, NH(CH$_2$)$_2$*C*H$_2$], 26.0 [t, NH$_2$(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$O], 25.9 [t, O(CH$_2$)$_2$-*C*H$_2$], 15.2 [t, O(CH$_2$)$_2$*C*H$_2$C≡CH] ppm. IR (ATR): $\tilde{\nu}$ = 3288 (N–H), 2940, 2911, 2866 (aliph. C–H), 1508 (C=C), 1474 (C–H), 1226, 1027 (C–O), 828 (1,4-disubstitution) cm^{-1}. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 468 [M + H]$^+$.

2-Chloro-*N*-[6-(4-{6-[4-(pent-4-ynyloxy)phenyloxy]hexyloxy}-phenyloxy)hexyl]acetamide (29): A solution of amine **28** (208 mg, 445 μmol) and anhydrous triethylamine (100 μL, 71.0 mg, 752 μmol) in anhydrous dichloromethane (54 mL) was cooled to –10 °C, and chloroacetyl chloride (50.0 μL, 71.0 mg, 629 μmol) in anhydrous dichloromethane (1 mL) was added. The reaction mixture was stirred for 4 h at room temperature and afterwards was washed with brine (2× 50 mL). The aqueous layer was extracted with dichloromethane (2× 50 mL) and the combined organic layers were dried with magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, chloroform/ethanol, 1:1, R_f = 0.87) to give **29** as a brownish solid (170 mg, 70%); m.p. 114 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.82 (s, 4 H, Ar^1-2,3,5,6-H or Ar^2-2,3,5,6-H), 6.81 (s, 4 H, Ar^1-2,3,5,6-H or Ar^2-2,3,5,6-H), 6.57 (br. s, 1 H, N*H*), 4.04 (s, 2 H, ClCH_2), 4.01 [t, ^3J = 6.1 Hz, 2 H, OCH_2(CH$_2$)$_2$-C≡CH], 3.93–3.87 (m, 6 H, OCH_2), 3.32 (m$_c$, 2 H, NHCH_2), 2.40 [td, ^3J_t = 7.0 Hz, ^4J_d = 2.6 Hz, 2 H, O(CH$_2$)$_2$CH_2C≡CH], 2.01–1.94 (m, 3 H, OCH$_2$CH_2CH$_2$C≡C*H*), 1.83–1.71 (m, 6 H, OCH$_2$CH_2), 1.58 (quint, ^3J = 7.4 Hz, 2 H, NHCH$_2$CH_2) 1.55–1.45 [m, 6 H, O(CH$_2$)$_2$CH_2], 1.45–1.35 [m, 2 H, NH(CH$_2$)$_2$CH_2] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.7 (s, *C*ONH), 153.3, 153.2, 153.1, 153.0 (4s, Ar^1-*C*-1,4, Ar^2-*C*-1,4), 115.5, 115.4, 115.4 (3d, Ar^1-*C*-2,3,5,6, Ar^2-*C*-2,3,5,6), 83.6 (s, *C*≡CH), 68.7 (d, C≡*C*H), 68.5, 68.4 (2t, O*C*H$_2$), 66.8 [t, O*C*H$_2$(CH$_2$)$_2$C≡CH], 42.7 (t, NH$_2$*C*H$_2$), 39.8 (t, Cl*C*H$_2$), 29.3, 29.3 (2t, OCH$_2$*C*H$_2$), 29.2 (t, NHCH$_2$*C*H$_2$), 28.3 (t, OCH$_2$*C*H$_2$CH$_2$C≡CH), 26.6 [t, NH(CH$_2$)$_2$*C*H$_2$], 25.9 [t, O(CH$_2$)$_2$*C*H$_2$], 15.2 [t, O(CH$_2$)$_2$*C*H$_2$C≡CH] ppm. IR (ATR): $\tilde{\nu}$ = 3291 (C≡C–H), 2940, 2867 (aliph. C–H), 1648, 1547 (C=O), 1508 (C=C), 1474 (C–H), 1226, 1027 (C–O), 828 (1,4-disubstitution), 770 (C–Cl) cm^{-1}. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 543 [M]$^{+\cdot}$. MS (ESI, $CHCl_3$, MeOH): *m*/*z* = 568, 566 [M + Na]$^+$. $C_{31}H_{42}$-$ClNO_5$ (543.28): C 68.43, H 7.78, N 2.57. $C_{31}H_{42}ClNO_5$·0.5H$_2$O (552.28): calcd. C 67.31, H 7.84, N 2.53; found C 67.18, H 7.57, N 2.51.

(1-{2-Oxo-2-[6-(4-{6-[4-(pent-4-ynyloxy)phenyloxy]hexyloxy}-phenyloxy)hexyl]amino}ethyl)-3-{4-[tris(4-*tert*-butylphenyl)-methyl]phenyl}pyridinium Iodide (30): A mixture of pyridine **11** (600 mg, 1.06 mmol), alkyne linker **29** (576 mg, 1.06 mmol) and sodium iodide (247 mg, 1.65 mmol) in 1,4-dioxane (70 mL) was heated to reflux for 2 d. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, dichloromethane/methanol, 20:1, R_f = 0.15) to obtain **30** as an orange solid (843 mg, 66%); m.p. 184 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.38 (br. s, 1 H, Py-2-H), 9.07 (d, ^3J = 6.0 Hz, 1 H, Py-6-H), 8.53–8.47 (m, 2 H, Py-4-H, CON*H*), 7.95 (dd, ^3J = 8.2 Hz, ^3J = 6.0 Hz, 1 H, Py-5-H), 7.60 (d, ^3J = 8.6 Hz, 2 H, Ar^2-2,6-H), 7.44 (d, ^3J = 8.6 Hz, 2 H, Ar^2-3,5-H), 7.26 (d, ^3J = 8.6 Hz, 6 H, Ar^1-3,5-H), 7.10 (d, ^3J = 8.6 Hz, 6 H, Ar^1-2,6-H), 6.82, 6.79 (2s, 8 H, Ar^3-2,3,5,6-H, Ar^4-2,3,5,6-H), 5.95 (s, 2 H,

PyCH_2), 4.01 [t, ^3J = 6.0 Hz, 2 H, Ar^{4}OCH_2(CH$_2$)$_2$C≡CH], 3.90 [m$_c$, 4 H, Ar^{3}OCH_2(CH$_2$)$_4$CH_2OAr^4], 3.86 [t, ^3J = 6.4 Hz, 2 H, NH(CH$_2$)$_5$CH_2OAr^3], 3.28 [m$_c$, 2 H, NHCH_2(CH$_2$)$_5$OAr^3], 2.39 [td, ^3J_t = 7.0, ^4J_d = 2.6 Hz, 2 H, Ar^{4}O(CH$_2$)$_2$CH_2C≡CH], 2.00–1.94 (m, 3 H, Ar^{4}OCH$_2$CH_2CH$_2$C≡C*H*), 1.81–1.75 [m, 4 H, Ar^{3}OCH$_2$CH_2(CH$_2$)$_2$CH_2CH$_2$OAr^4], 1.73 [m$_c$, 2 H, NH(CH$_2$)$_4$-CH_2CH$_2$OAr^3], 1.67–1.60 [m, 2 H, NHCH$_2$CH_2(CH$_2$)$_4$OAr^3], 1.54–1.49 [m, 4 H, Ar^{3}O(CH$_2$)$_2$CH_2CH_2(CH$_2$)$_2$OAr^4], 1.47–1.39 [m, 4 H, NH(CH$_2$)$_2$CH_2CH_2(CH$_2$)$_2$OAr^3], 1.31 [s, 27 H, C(CH_3)$_3$] ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 163.0 (s, *C*ONH), 153.3, 153.2, 153.1, 153.0 (4s, Ar^3-*C*-1,4, Ar^4-*C*-1,4), 151.2 (s, Ar^2-*C*-4), 148.8 (s, Ar^1-*C*-4), 143.2 (d, Py-*C*-2), 143.1 (s, Ar^1-*C*-1), 142.8 (d, Py-*C*-6), 142.5 (d, Py-*C*-4), 141.4 (d, Py-*C*-3), 132.8 (d, Ar^2-*C*-3,5), 130.6 (d, Ar^1-*C*-2,6), 129.3 (s, Ar^2-*C*-1), 127.5 (d, Py-*C*-5), 126.3 (d, Ar^2-*C*-2,6), 124.4 (d, Ar^1-*C*-3,5), 115.5, 115.4, 115.4 (3d, Ar^3-*C*-2,3,5,6, Ar^4-*C*-2,3,5,6), 83.6 (s, *C*≡CH), 68.8 (d, C≡*C*H), 68.5, 68.5 (2t, O*C*H$_2$), 66.8 [t, Ar^{4}O*C*H$_2$(CH$_2$)$_2$C≡CH], 63.7 [s, *C*(Ar^1)$_3$Ar^2], 62.5 (t, Py*C*H$_2$), 40.3 [t, NH*C*H$_2$(CH$_2$)$_5$OAr^3], 34.3 [s, *C*(CH$_3$)$_3$], 31.4 [q, C(*C*H$_3$)$_3$], 29.3 [t, Ar^{3}OCH$_2$*C*H$_2$(CH$_2$)$_2$*C*H$_2$CH$_2$OAr^4], 29.2 [t, NH(CH$_2$)$_4$*C*H$_2$CH$_2$OAr^3], 28.8 [t, NHCH$_2$*C*H$_2$(CH$_2$)$_4$OAr^3], 28.3 (t, Ar^{4}OCH$_2$*C*H$_2$CH$_2$C≡CH), 26.7 [t, NH(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$OAr^3], 25.9 [t, Ar^{3}O(CH$_2$)$_2$*C*H$_2$*C*H$_2$(CH$_2$)$_2$OAr^4], 25.6 [t, NH(CH$_2$)$_2$*C*H$_2$-(CH$_2$)$_3$OAr^3], 15.2 [t, Ar^{4}O(CH$_2$)$_2$*C*H$_2$C≡CH] ppm. IR (ATR): $\tilde{\nu}$ = 3296 (C≡C–H), 3220, 3054 (N–H), 2940, 2906, 2861 (aliph. C–H), 1677 (C=O),1507 (C=C), 1472 (C–H), 1227, 1018 (C–O), 824 (1,4-disubstitution) cm^{-1}. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 1074 [M – I]$^+$. $C_{73}H_{89}IN_2O_5$ (1200.58): C 72.98, H 7.47, N 2.33. $C_{73}H_{89}IN_2O_5$·2.5H_2O (1245.61): calcd. C 70.34, H 7.60, N 2.25; found C 70.38, H 7.48, N 2.19.

(1-{2-Oxo-2-[6-(4-{6-[4-(pent-4-ynyloxy)phenyloxy]hexyloxy}-phenyloxy)hexyl]amino}ethyl)-3-{4-[tris(4-*tert*-butylphenyl)methyl]-phenyl}pyridinium Hexafluorophosphate (31): Pyridinium iodide **30** (843 mg, 702 μmol) was dissolved in anhydrous dichloromethane (10 mL), and silver(I) hexafluorophosphate (195 mg, 772 μmol) in anhydrous dichloromethane (4 mL) was added. The mixture was stirred for 2 h at room temperature and filtered afterwards. The filtrate was concentrated under reduced pressure and the crude product was purified by column chromatography (silica gel, dichloromethane/methanol, 20:1, R_f = 0.21) to give **31** as an orange solid (495 mg, 58%); m.p. 150 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.81 (s, 1 H, Py-2-H), 8.71 (br. s, 1 H, Py-6-H), 8.36 (d, ^3J = 7.8 Hz, 1 H, Py-4-H), 7.91 (br. s, 1 H, Py-5-H), 7.54 (br. s, 1 H, CON*H*), 7.45 (d, ^3J = 8.4 Hz, 2 H, Ar^2-2,6-H), 7.39 (d, ^3J = 8.4 Hz, 2 H, Ar^2-3,5-H), 7.25 (d, ^3J = 8.6 Hz, 6 H, Ar^1-3,5-H), 7.09 (d, ^3J = 8.6 Hz, 6 H, Ar^1-2,6-H), 6.81 (m$_c$, 4 H, Ar^4-2,3,5,6-H)*, 6.77 (s, 4 H, Ar^3-*H*-2,3,5,6)*, 5.43 (s, 2 H, PyCH_2), 4.00 [t, ^3J = 6.0 Hz, 2 H, Ar^{4}OCH_2(CH$_2$)$_2$C≡CH], 3.88 [m$_c$, 4 H, Ar^{3}OCH_2(CH$_2$)$_4$CH_2-OAr^4], 3.83 [t, ^3J = 6.5 Hz, 2 H, NH(CH$_2$)$_5$CH_2OAr^3], 3.24 [m$_c$, 2 H, NHCH_2(CH$_2$)$_5$OAr^3], 2.39 [td, ^3J_t = 7.0 Hz, ^4J_d = 2.6 Hz, 2 H, Ar^{4}O(CH$_2$)$_2$CH_2C≡CH], 2.00–1.94 (m, 3 H, Ar^{4}OCH$_2$CH_2CH$_2$-C≡C*H*), 1.81–1.73 [m, 4 H, Ar^{3}OCH$_2$CH_2(CH$_2$)$_2$CH_2CH$_2$OAr^4], 1.69 [m$_c$, 2 H, NH(CH$_2$)$_4$CH_2CH$_2$OAr^3], 1.60–1.52 [m, 2 H, NHCH$_2$CH_2(CH$_2$)$_4$OAr^3], 1.50 [m$_c$, 4 H, Ar^{3}O(CH$_2$)$_2$CH_2CH_2-(CH$_2$)$_2$OAr^4], 1.45–1.33 [m, 4 H, NH(CH$_2$)$_2$CH_2CH_2(CH$_2$)$_2$OAr^3], 1.29 [s, 27 H, C(CH_3)$_3$] ppm. *The assignment may be inverted. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 163.2 (s, *C*ONH), 153.3, 153.2, 153.1, 153.0 (4s, Ar^3-*C*-1,4, Ar^4-*C*-1,4), 150.8 (s, Ar^2-*C*-4), 148.8 (s, Ar^1-*C*-4), 143.3 (d, Py-*C*-6), 143.2 (d, Py-*C*-2), 143.2 (s, Ar^1-*C*-1), 142.6 (Py-*C*-4), 141.2 (s, Py-*C*-3), 132.6 (d, Ar^2-*C*-3,5), 130.6 (d, Ar^1-*C*-2,6), 129.8 (s, Ar^2-*C*-1), 127.7 (d, Py-*C*-5), 126.2 (d, Ar^2-*C*-2,6), 124.4 (d, Ar^1-*C*-3,5), 115.5, 115.4, 115.4 (3d, Ar^3-*C*-2,3,5,6, Ar^4-*C*-2,3,5,6), 83.6 (s, *C*≡CH), 68.8 (d, C≡*C*H), 68.5, 68.5 (2t, O*C*H$_2$), 66.8 [t, Ar^{4}O*C*H$_2$(CH$_2$)$_2$C≡CH], 63.7 [s, *C*(Ar^1)$_3$Ar^2], 62.5 (t, Py*C*H$_2$), 40.3 [t, NH*C*H$_2$(CH$_2$)$_5$OAr^3], 34.3 [s, *C*(CH$_3$)$_3$], 31.4 [q, C(*C*H$_3$)$_3$], 29.4, 29.3 [2t, Ar^{3}OCH$_2$*C*H$_2$(CH$_2$)$_2$*C*H$_2$CH$_2$OAr^4], 29.2 [t, NH(CH$_2$)$_4$*C*H$_2$CH$_2$OAr^3], 28.8 [t, NHCH$_2$*C*H$_2$(CH$_2$)$_4$-OAr^3], 28.3 (t, Ar^{4}OCH$_2$*C*H$_2$CH$_2$C≡CH), 26.5 [t, NH(CH$_2$)$_2$-*C*H$_2$(CH$_2$)$_3$OAr^3], 25.9 [t, Ar^{3}O(CH$_2$)$_2$*C*H$_2$*C*H$_2$(CH$_2$)$_2$OAr^4], 25.6 [t, NH(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_2$OAr^3], 15.2 [t, Ar^{4}O(CH$_2$)$_2$*C*H$_2$-C≡CH] ppm. IR (ATR): $\tilde{\nu}$ = 3292 (C≡C–H), 2943, 2866 (aliph. C–H), 1692 (C=O),1507 (C=C), 1472 (C–H), 1228, 1018 (C–O), 824 (1,4-disubstitution) cm^{-1}. MS (MALDI-TOF, Cl-CCA): *m*/*z* = 1073 [M – PF$_6$]$^+$. $C_{73}H_{89}F_6N_2O_5P$ (1218.64): C 71.90, H 7.36, N 2.30. $C_{73}H_{89}F_6N_2O_5P$·1.7H_2O (1249.26): calcd. C 70.14, H 7.45, N 2.24; found C 69.94, H 7.15, N 2.30.

[2]-{[1-(2-Oxo-2-{[6-(4-{6-[4-(3-{1-[6-(3,3,3-tris)4-*tert*-butylphenyl]-propyloxy}-6-oxohexyl)-1,2,3-triazol-4-yl]propyloxy}phenyloxy)-hexyloxy]phenyloxy}hexyl)amino]ethyl{-3-[4-(tris)4-*tert*-butyl-phenyl]methyl}phenyl}pyridinium-hexafluorophosphat[-*rotaxa*-(5^4-methoxy-3,7,10,21-tetraoxa-1,9)1,4(-dibenzena-5)2,6]-pyridina-heneicosaphan} (32): To a solution of macrocycle **2** (101 mg, 195 μmol), alkyne half-axis **31** (237 mg, 195 μmol) and azide half-axis **7** (116 mg, 195 μmol) in anhydrous dichloromethane (10 mL) copper(I) tetrakisacetonitrilo hexafluorophosphate (72.7 mg, 195 μmol) was added, and the reaction mixture was stirred for 2 d at room temperature. The mixture was diluted with dichloromethane (20 mL) and methanol (10 mL), and potassium cyanide (60 mg, 922 μmol) in methanol (10 mL) was added. After stirring for 1 h, the solvents were removed under reduced pressure and dichloromethane (10 mL) was added. The solution was washed with water (10 mL) and the aqueous layer was extracted with dichloromethane (10 mL). The combined organic layer was dried with magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by column chromatography [silica gel, gradient: dichloromethane/methanol, 40:1 to 10:1, R_f = 0.13 (40:1)] to afford rotaxane **32** (33.5 mg, 7%) and axis **33** (99.4 mg, 28%) as orange solids.

Rotaxane 32: ^{1}H NMR (600 MHz, CDCl$_3$): δ = 8.70 (s, 1 H, Py^1-2-H), 7.90 (d, ^3J = 8.1 Hz, 1 H, Py^1-4-H), 7.80 (d, ^3J = 6.1 Hz, 1 H, Py^1-6-H), 7.49 (dd, ^3J = 8.1, ^3J = 6.1 Hz, 1 H, Py^1-5-H), 7.33–7.28 (m, 8 H, Ar^2-3,5-H, Ar^1-3,5-H), 7.27–7.23 (m, 7 H, triazol-5-H, Ar^5-3,5-H), 7.20–7.15 (m, 12 H, Ar^1-2,6-H, Ar^5-2,6-H), 7.14 (d, ^3J = 8.4 Hz, 2 H, Ar^2-2,6-H), 7.01 (m$_c$, 1 H, CON*H*), 6.86 (d, ^3J = 8.5 Hz, 4 H, Ar^6-3,5-H), 6.82 (s, 2 H, Py^2-3,5-H), 6.81 (s, 8 H, Ar^3-2,3,5,6-H, Ar^4-2,3,5,6-H), 6.31 (d, ^3J = 8.5 Hz, 4 H, Ar^6-2,6-H), 5.00 (s, 2 H, Py^{1}CH_2CONH), 4.43 (d, ^2J = 10.6 Hz, 2 H, Py^{2}CH$_2$OCH_aH$_b$Ar^6), 4.37 (d, ^2J = 11.6 Hz, 2 H, Py^{2}CH_aH$_b$-OCH$_2$Ar^6), 4.34 (d, ^2J = 10.6 Hz, 2 H, Py^{2}CH$_2$OCH$_a$$H_b$Ar^6), 4.31 (d, ^2J = 11.6 Hz, 2 H, Py^{2}CH$_a$$H_bOCH_2$Ar^6), 4.29 [t, ^3J = 7.1 Hz, 2 H, triazol-CH_2(CH$_2$)$_4$COO], 3.94 [t, ^3J = 6.1 Hz, 2 H, Ar^{4}OCH_2(CH$_2$)$_2$triazol], 3.92–3.85 [m, 8 H, CH_2OAr^{3}OCH_2(CH$_2$)$_4$-CH_2OAr^4, COOCH_2CH$_2$], 3.83 (s, 3 H, Py^{2}OCH_3), 3.69 (t, ^3J = 6.1 Hz, 4 H, Ar^{6}OCH_2), 3.07 (q, ^3J = 6.6 Hz, 2 H, NHCH_2), 2.92–2.85 [m, 4 H, Ar^{4}O(CH$_2$)$_2$CH_2triazol, COOCH$_2$CH_2], 2.22 [t, ^3J = 7.5 Hz, 2 H, triazol-(CH$_2$)$_4$CH_2COO], 2.13 (quint, ^3J = 7.3 Hz, 2 H, Ar^{4}OCH$_2$CH_2CH$_2$triazol), 1.87 [quint, ^3J = 7.5 Hz, 2 H, triazol-CH$_2$CH_2(CH$_2$)$_3$COO], 1.81–1.75 [m, 4 H, Ar^{3}OCH$_2$CH_2(CH$_2$)$_2$-CH_2CH$_2$OAr^4], 1.71 [quint, 2 H, NH(CH$_2$)$_4$CH_2CH$_2$OAr^3], 1.68–1.59 [m, 6 H, Ar^{6}OCH$_2$CH_2, triazol-(CH$_2$)$_3$CH_2CH$_2$COO], 1.53–1.48 [m, 4 H, Ar^{3}O(CH$_2$)$_2$CH_2CH_2(CH$_2$)$_2$OAr^4], 1.45–1.34 [m, 8 H, NHCH$_2$CH_2CH$_2$CH_2 (CH$_2$)$_2$OAr^3, Ar^{6}O(CH$_2$)$_2$CH_2], 1.34–1.25 [m, 12 H, Ar^{6}O(CH$_2$)$_3$CH_2CH_2, NH(CH$_2$)$_2$CH_2, triazol-(CH$_2$)$_2$-CH_2(CH$_2$)$_2$COO], 1.31, 1.29 [2s, 54 H, C(CH_3)$_3$] ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ = 173.4 (s, *C*OOCH$_2$), 167.2 (s, Py^2-*C*-4), 163.0 (s, *C*ONH), 158.8 (s, Py^2-*C*-2,6), 158.4 (s, Ar^6-*C*-1), 153.3, 153.2, 153.0 (3s, Ar^3-*C*-1,4, Ar^4-*C*-1,4), 150.5 (s, Ar^2-*C*-4), 148.8 (s,

Ar[1]-*C*-4), 148.5 (s, Ar[5]-*C*-4), 147.3 (s, triazol-*C*-4), 144.9 (d, Py[1]-*C*-2), 143.8 (s, Ar[5]-*C*-1), 143.4 (s, Ar[1]-*C*-1), 141.9 (d, Py[1]-*C*-6)*, 140.5 (d, Py[1]-*C*-4)*, 139.6 (s, Py[1]-*C*-3)*, 131.8 (d, Ar[2]-*C*-3,5), 130.5 (d, Ar[1]-*C*-2,6), 130.1 (d, Ar[6]-*C*-3,5), 129.1 (s, Ar[2]-*C*-1), 129.0 (s, Ar[6]-*C*-4)*, 128.5 (d, Ar[5]-*C*-2,6), 126.2 (d, Ar[2]-*C*-2,6), 125.7 (d, Py[1]-*C*-5), 124.7 (d, Ar[5]-*C*-3,5), 124.5 (d, Ar[1]-*C*-3,5), 120.8 (d, triazol-*C*-5), 115.4 (d, Ar[3]-*C*-2,3,5,6, Ar[4]-*C*-2,3,5,6), 113.9 (d, Ar[6]-*C*-2,6), 107.7 (d, Py[2]-*C*-3,5), 73.0 (t, Ar[6]*C*H$_2$O), 72.6 (t, Py[2]*C*H$_2$O), 68.5 [t, Ar[3]O*C*H$_2$(CH$_2$)$_4$*C*H$_2$OAr[4]], 68.4 [t, NH(CH$_2$)$_5$*C*H$_2$OAr[3]], 67.5 [t, Ar[4]O*C*H$_2$(CH$_2$)$_2$triazol], 67.1 (t, Ar[6]O*C*H$_2$), 63.8 [s, *C*(Ar[1])$_3$], 63.0 (t, COO*C*H$_2$CH$_2$), 61.7 (t, Py[1]*C*H$_2$), 55.4 (q, Py[2]O*C*H$_3$), 53.7 [s, *C*(Ar[5])$_3$], 49.9 [t, triazol-*C*H$_2$(CH$_2$)$_4$COO], 40.1 (t, NH*C*H$_2$), 38.7 (t, COOCH$_2$*C*H$_2$), 34.4, 34.3 [2s, *C*(CH$_3$)$_3$], 33.9 [t, triazol-(CH$_2$)$_4$*C*H$_2$COO], 31.4 [q, C(*C*H$_3$)$_3$], 30.1 [t, triazol-CH$_2$*C*H$_2$(CH$_2$)$_3$-COO], 29.4 [t, Ar[6]O(CH$_2$)$_3$*C*H$_2$*C*H$_2$][#], 29.3 [t, Ar[3]OCH$_2$*C*H$_2$-(CH$_2$)$_2$ *C*H$_2$CH$_2$OAr[4]][#], 29.2 [t, NH(CH$_2$)$_4$*C*H$_2$CH$_2$OAr[3]][#], 29.1 (t, Ar[4]OCH$_2$*C*H$_2$CH$_2$triazol)[#], 28.8 (t, NHCH$_2$*C*H$_2$)[#], 28.6 (t, Ar[6]OCH$_2$*C*H$_2$)[#], 26.6 [t, NH(CH$_2$)$_2$*C*H$_2$][#], 26.0 [t, triazol-(CH$_2$)$_2$-*C*H$_2$(CH$_2$)$_2$COO][#], 25.9 [t, Ar[3]O(CH$_2$)$_2$CH$_2$CH$_2$(CH$_2$)$_2$OAr[4]][#], 25.9 [t, Ar[6]O(CH$_2$)$_2$CH$_2$][#], 25.7 [t, NH(CH$_2$)$_3$CH$_2$(CH$_2$)$_2$OAr[3]][#], 24.2 [t, triazol-(CH$_2$)$_3$CH$_2$CH$_2$COO], 22.2 [t, Ar[4]O(CH$_2$)$_2$CH$_2$triazol] ppm. *The signal is only observed in the HMBC spectrum. [#]The signals were assigned by comparison with axis **33** and macrocycle **2**. MS (MALDI-TOF, Cl-CCA): *m/z* = 2190 [M – PF$_6$]$^+$. HRMS (FT-ICR): *m/z* calcd. for $C_{144}H_{183}N_6O_{12}^+$ 2188.3888 [M]$^+$, 1094.6980 [M + H]$^{2+}$; found 2188.3863 [M]$^+$, 1094.6986 [M + H]$^{2+}$.

Axis 33: M.p. 112 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.88 (br. s, 1 H, Py[1]-2-H), 8.65 (d, ^3J = 6.0 Hz, 1 H, Py[1]-6-H), 8.48 (d, ^3J = 8.2 Hz, 1 H, Py[1]-4-H), 7.93 (dd, ^3J = 6.0, ^3J = 8.2 Hz, 1 H, Py[1]-5-H), 7.49 (d, ^3J = 8.7 Hz, 2 H, Ar[2]-2,6-H), 7.42 (d, ^3J = 8.7 Hz, 2 H, Ar[2]-3,5-H), 7.37 (br. s, 1 H, CON*H*), 7.28–7.23 (m, 13 H, Ar[1]-3,5-H, Ar[5]-3,5-H, triazol-5-H), 7.17 (d, ^3J = 8.7 Hz, 6 H, Ar[5]-2,6-H), 7.10 (d, ^3J = 8.7 Hz, 6 H, Ar[1]-2,6-H), 6.80, 6.79 (2s, 8 H, Ar[3]-2,3,5,6-H, Ar[4]-2,3,5,6-H), 5.40 (s, 2 H, Py[1]C*H*$_2$), 4.29 [t, ^3J = 7.2 Hz, 2 H, triazol-C*H*$_2$(CH$_2$)$_4$COO], 3.94 [t, ^3J = 6.2 Hz, 2 H, Ar[4]OC*H*$_2$(CH$_2$)$_2$triazol], 3.92–3.84 [m, 8 H, C*H*$_2$OAr[3]OC*H*$_2$(CH$_2$)$_4$-C*H*$_2$OAr[4], COOC*H*$_2$CH$_2$], 3.28 (m$_c$, 2 H, NHC*H*$_2$), 2.88 [m$_c$, 4 H, Ar[4]O(CH$_2$)$_2$C*H*$_2$triazol, COOCH$_2$C*H*$_2$], 2.23 (t, ^3J = 7.5 Hz, 2 H, C*H*$_2$COOCH$_2$), 2.13 (m$_c$, 2 H, Ar[4]OCH$_2$C*H*$_2$CH$_2$triazol), 1.88 [quint, ^3J = 7.5 Hz, 2 H, triazol-CH$_2$C*H*$_2$(CH$_2$)$_3$COO], 1.82–1.70 [m, 6 H, C*H*$_2$CH$_2$OAr[3]OCH$_2$C*H*$_2$(CH$_2$)$_2$C*H*$_2$CH$_2$O], 1.68–1.56 [m, 4 H, triazol-(CH$_2$)$_3$C*H*$_2$CH$_2$COO, NHCH$_2$C*H*$_2$], 1.54–1.47 [m, 6 H, C*H*$_2$(CH$_2$)$_2$OAr[3]O(CH$_2$)$_2$C*H*$_2$C*H*$_2$], 1.39–1.24 [m, 4 H, triazol-(CH$_2$)$_2$C*H*$_2$(CH$_2$)$_2$COO, NH(CH$_2$)$_2$C*H*$_2$], 1.30, 1.29 [2s, 54 H, C(C*H*$_3$)$_3$] ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 173.4 (s, *C*O-OCH$_2$), 162.9 (s, *C*ONH), 153.3, 153.2, 153.1, 153.0 (4s, Ar[3]-*C*-1,4, Ar[4]-*C*-1,4), 151.1 (s, Ar[2]-*C*-4), 148.8 (s, Ar[1]-*C*-4), 148.5 (s, Ar[5]-*C*-4), 147.3 (s, triazol-*C*-4), 143.8 (s, Ar[5]-*C*-1), 143.3 (d, Py[1]-*C*-2), 143.1 (s, Ar[1]-*C*-1), 142.9 (d, Py[1]-*C*-6), 142.7 (d, Py[1]-*C*-4), 141.6 (s, Py[1]-*C*-3), 132.8 (d, Ar[2]-*C*-3,5), 130.6 (d, Ar[1]-*C*-2,6), 129.5 (s, Ar[2]-*C*-1), 128.5 (d, Ar[5]-*C*-2,6), 127.6 (d, Py[1]-*C*-5), 126.2 (d, Ar[2]-*C*-2,6), 124.7 (d, Ar[5]-*C*-3,5), 124.4 (d, Ar[1]-*C*-3,5), 120.8 (d, triazol-*C*-5), 115.4, 115.4 (2d, Ar[3]-*C*-2,3,5,6, Ar[4]-*C*-2,3,5,6), 68.5, 68.4 [2t, *C*H$_2$OAr[3]O*C*H$_2$(CH$_2$)$_4$*C*H$_2$OAr[4]], 67.5 [t, Ar[4]O*C*H$_2$(CH$_2$)$_2$triazol], 63.7 [s, *C*(Ar[1])$_3$], 62.9 (t, COO*C*H$_2$CH$_2$), 62.5 (t, Py[1]*C*H$_2$), 53.7 [s, *C*(Ar[5])$_3$], 49.9 [t, triazol-*C*H$_2$(CH$_2$)$_4$COO], 40.4 (t, NH*C*H$_2$), 38.7 (t, COOCH$_2$*C*H$_2$), 34.3, 34.3 [2s, *C*(CH$_3$)$_3$], 33.9 (t, *C*H$_2$COO), 31.3 [q, C(*C*H$_3$)$_3$], 30.0 [t, triazol-CH$_2$*C*H$_2$(CH$_2$)$_3$COO], 29.3 [t, Ar[3]OCH$_2$*C*H$_2$ (CH$_2$)$_2$*C*H$_2$CH$_2$OAr[4]], 29.2 [t, NH(CH$_2$)$_4$*C*H$_2$CH$_2$-OAr[3]], 29.0 (t, Ar[4]OCH$_2$*C*H$_2$CH$_2$-triazol), 28.8 (t, NHCH$_2$*C*H$_2$), 26.5 [t, NH(CH$_2$)$_2$*C*H$_2$], 26.0 [t, triazol-(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_2$COO], 25.9 [t, Ar[3]O(CH$_2$)$_2$*C*H$_2$*C*H$_2$(CH$_2$)$_2$OAr[4]]*, 25.6 [t, NH(CH$_2$)$_3$-*C*H$_2$(CH$_2$)$_2$OAr[3]]*, 24.2 (t, *C*H$_2$CH$_2$COO), 22.2 [t, Ar[4]O(CH$_2$)$_2$-*C*H$_2$triazol] ppm. *The assignment may be inverted. IR (ATR): $\tilde{\nu}$ = 2951, 2865 (aliph. C–H), 1731, 1693 (C=O), 1604, 1506 (C=C), 1464 (C–H), 1226, 1017 (C–O), 840 (isolated arom. H), 822 (1,4-disubstitution) cm^{-1}. MS (MALDI-TOF, Cl-CCA): *m/z* = 1670 [M]$^+$. HRMS (FT-ICR): *m/z* calcd. for $C_{112}H_{142}N_5O_7^+$ 1669.0903 [M]$^+$, 835.0488 [M + H]$^{2+}$; found 1669.0908 [M]$^+$, 835.0493 [M + H]$^{2+}$. $C_{112}H_{142}F_6N_5O_7P$ (1814.06): calcd. C 74.10, H 7.88, N 3.86; found C 73.91, H 8.19, N 4.12.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra for compounds **4**, **6**, **7**, **9**–**11**, **13**–**33**, HRMS of compounds **32** and **33**, and 2D NOESY spectra of **32** and protonated **32**.

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft (DFG) (Sonderforschungsbereich 677) is gratefully acknowledged. The authors thank the work group of Prof. Dr. Jürgen Grotemeyer for HRMS measurements.

[1] T. Kelly (Ed.), *Molecular Machines*, *Top. Curr. Chem.* vol. 262, Springer-Verlag, Berlin, Heidelberg, Germany, **2005**.
[2] V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines - Concepts and Perspectives for the Nanoworld*, 2nd ed., Wiley-VCH, Weinheim, Germany, **2008**.
[3] B. L. Feringa, W. R. Browne (Eds.), *Molecular Switches*, 2nd ed., Wiley-VCH, Weinheim, Germany, **2011**.
[4] P. D. Boyer, *Biochim. Biophys. Acta Bioenerg.* **1993**, *1140*, 215–250.
[5] J. Baudry, E. Tajkhorshid, F. Molnar, J. Phillips, K. Schulten, *J. Phys. Chem. B* **2001**, *105*, 915–918.
[6] G. Steinberg-Yfrach, P. A. Liddell, S.-C. Hung, A. L. Moore, D. Gust, T. A. Moore, *Nature* **1997**, *385*, 239–241.
[7] Whilst this manuscript was being revised, a light-driven proton pump across a macroscopic membrane was published, see: X. Xie, G. A. Crespo, G. Mistlberger, E. Bakker, *Nature Chem.* **2014**, *6*, 202–207.
[8] W. Vetter, G. Schill, *Tetrahedron* **1967**, *23*, 3079–3093.
[9] G. Schill, *Catenanes, Rotaxanes, and Knots*, Academic Press, New York, London, **1971**.
[10] J.-P. Sauvage, C. Dietrich-Buchecker (Eds.), *Molecular Catenanes, Rotaxanes and Knots – A journey through the world of molecular topology*, Wiley-VCH, Weinheim, Germany, **1999**.
[11] First switchable shuttle: R. A. Bissell, E. Córdova, A. E. Kaifer, J. F. Stoddart, *Nature* **1994**, *369*, 133–137.
[12] A.-M. L. Fuller, D. A. Leigh, P. J. Lusby, A. M. Z. Slawin, D. B. Walker, *J. Am. Chem. Soc.* **2005**, *127*, 12612–12619.
[13] U. Lüning, E. Mak, M. Zindler, B. Hartkopf, R. Herges, *Eur. J. Org. Chem.* **2010**, 4932–4940.
[14] One of many examples for bipyridinium ions in the axis, see: P. R. Ashton, R. Ballardini, V. Balzani, A. Credi, K. R. Dress, E. Ishow, C. J. Kleverlaan, O. Kocian, J. A. Preece, N. Spencer, J. F. Stoddart, M. Venturi, S. Wenger, *Chem. Eur. J.* **2000**, *6*, 3558–3574.
[15] A triazolium ion as part of the axis, see: V. Blanco, A. Carlone, K. D. Hänni, D. A. Leigh, B. Lewandowski, *Angew. Chem. Int. Ed.* **2012**, *51*, 5166–5169; *Angew. Chem.* **2012**, *124*, 5256–5259.
[16] A second example for a triazolium ion as part of the axis, see: G. T. Spence, M. B. Pitak, P. D. Beer, *Chem. Eur. J.* **2012**, *18*, 7100–7108.
[17] A pyridinium ion as part of the axis: E. Busseron, C. Romuald, F. Coutrot, *Chem. Eur. J.* **2010**, *16*, 10062–10073.
[18] A rotaxane with a pyridinium ion in the axis formed by a click reaction, see: T. Ogoshi, D. Yamafuji, T. Aoki, K. Kitajima, T. Yamagishi, Y. Hayashi, S. Kawauchi, *Chem. Eur. J.* **2012**, *18*, 7493–7500.

[19] V. Aucagne, K. D. Hänni, D. A. Leigh, P. J. Lusby, D. B. Walker, *J. Am. Chem. Soc.* **2006**, *128*, 2186–2187.
[20] K. D. Hänni, D. A. Leigh, *Chem. Soc. Rev.* **2010**, *39*, 1240–1251.
[21] S. Durot, P. Mobian, J.-P. Collin, J.-P. Sauvage, *Tetrahedron* **2008**, *64*, 8496–8503.
[22] For a quite similar rotaxane, but with a protonatable amine in the axis, see: H. Zheng, W. Zhou, J. Lv, X. Yin, Y. Li, H. Liu, Y. Li, *Chem. Eur. J.* **2009**, *15*, 13253–13262.
[23] F. Huang, K. A. Switek, H. W. Gibson, *Chem. Commun.* **2005**, 3655–3657.
[24] S.-Z. Hu, C.-F. Chen, *Chem. Eur. J.* **2011**, *17*, 5424–5431.
[25] W. Zhang, H. Yamamoto, *J. Am. Chem. Soc.* **2007**, *129*, 286–287.
[26] J. P. Collman, S. E. Groh, *J. Am. Chem. Soc.* **1982**, *104*, 1391–1403.
[27] H. W. Gibson, S.-H. Lee, P. T. Engen, P. Lecavalier, J. Sze, Y. X. Shen, M. Bheda, *J. Org. Chem.* **1993**, *58*, 3748–3756.
[28] W. Li, D. P. Nelson, M. S. Jensen, R. S. Hoerrner, D. Cai, R. D. Larsen, *Org. Synth.* **2005**, *81*, 89–97.

Received: March 12, 2014
Published Online: May 7, 2014

