Experimental Section

3: All reactions were carried out in the presence of a small amount of BHT and, except for the lipoxygenase-catalyzed hydroperoxidation, under a nitrogen atmosphere. Methyl peracetal acid **7** was prepared from DHA as previously described for linoleic acid,[2a] and isolated by flash column chromatography, followed by drying over $MgSO_4$. After filtration, the solvent was evaporated at below 30 °C, and the resulting **7** (ca. 0.15 g, 0.4 mmol) dissolved in ethanol-free chloroform, followed by the addition of DCC (0.2 g, 0.9 mmol), dimethylaminopyridine (0.012 g, 0.09 mmol) and lyso-PC **8** (0.15 g, 0.3 mmol). The reaction mixture was stirred at room temperature for 48 h, and the product purified on a silica gel column ($CHCl_3$/MeOH/NH_3 (aq.) 60:30:1 to 50:30:3) to give phospholipid **9** (0.09 g, 30 % from **8**), which was then dissolved in THF/AcOH/H_2O (4:2:1) and stirred for 24 h, which achieved complete deprotection of the hydroperoxy group. The product thus obtained was purified by reversed-phase chromatography (ODS, $CHCl_3$/MeOH/H_2O, 4.5:100:5) to give high-purity **3** as a resinous solid (0.065 g, 7 % from **5**). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.88$ (t, 3H; ω-CH_3), 0.95 (t, 3H; ω'-CH_3), 1.26 (m, 32H; $OCO(CH_2)_{16}CH_3$), 2.03 (m, 2H; H21′), 2.28 (m, 1H; one proton of C18′), 2.39 (m, 4H; H2′ and H3′), 2.46 (m, 1H; one proton of C18′), 2.87 (m, 4H; H6′ and H9′), 2.98 (m, 2H; H12′), 3.28 (s, 9H; $N(CH_3)_3$), 3.72 (m, 2H; OCH_2CH_2N), 3.97 (m, 2H; CH_2OP), 4.18 (m, 1H; one proton of $OCH_2CH(OR)CH_2OP$), 4.30 (m, 2H; OCH_2CH_2N), 4.38 (m, 2H; H17′, one proton of $OCH_2CH(OR)CH_2OP$), 5.24 (br s, 1H; $OCH_2CH(OR)CH_2$-OP), 5.42 (m, 9H; H4′, H5′, H7′, H8′, H10′, H11′, H13′, H19′, H20′), 5.64 (dd, $J = 15$, 8 Hz, 1H; H16′), 6.10 (t, $J = 11$ Hz, 1H; H14′), 6.58 (dd, $J = 11$, 15 Hz, 1H; H15′); ES-MS: found: m/z: 866.6; calcd for $[C_{48}H_{84}NO_{10}P+H^+]$: m/z: 866.6.

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Gel-Phase MAS NMR Spectroscopy of a Polymer-Supported Pseudorotaxane and Rotaxane: Receptor Binding to an "Inert" Polyethylene Glycol Spacer**

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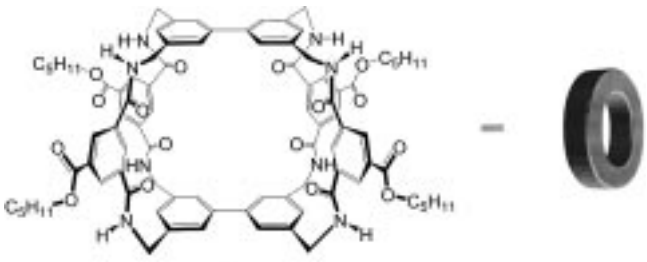
The combination of magic-angle spinning (MAS) and high-resolution probe technology has provided chemists with a powerful technique for obtaining solutionlike ^{1}H NMR spectra of resin-bound samples.[1] As previously described, we have been successful in applying gel-phase MAS spectroscopy to the study of metal – ligand interactions at the solid – liquid interface.[2] Following this success, we set out to extend our understanding of other interactions, such as those between the tricyclic polyamide receptor **1** and carbohydrates. However, during the course of this study, we discovered an unexpected phenomenon which led to the synthesis of a resin-bound rotaxane as described below.



1

Macrocycle **1** is a good receptor for octyl pyranosides.[3] Therefore, a galactose residue was attached onto ArgoGel resin through the primary hydroxide group, so that **1** would bind to the sugar unit and allow us to study the binding between the solid and liquid interfaces. ArgoGel resins contain highly flexible polyethylene glycol (PEG) chains (30 – 40 units) appended to a 1 % cross-linked polystyrene bead; the flexibility of these PEG chains allows us to obtain solutionlike NMR spectra using MAS techniques. An NMR titration was performed to investigate for possible binding between **1** and the solid-supported galactoside. However, this titration unexpectedly showed a splitting of the PEG reso-

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nance (Figure 1). Since the binding between the macrocycle and the sugar is reversible, there might be a possibility that the macrocycle could dissociate from the sugar unit into the PEG

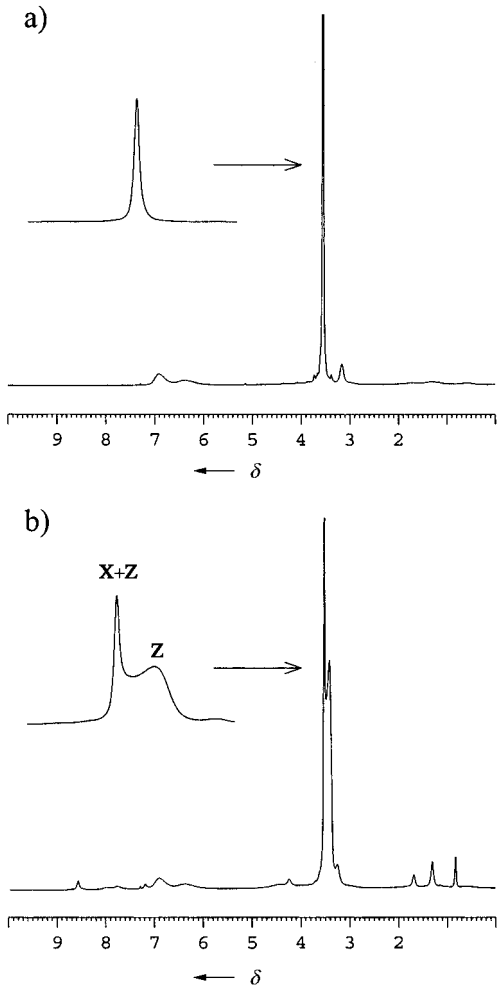
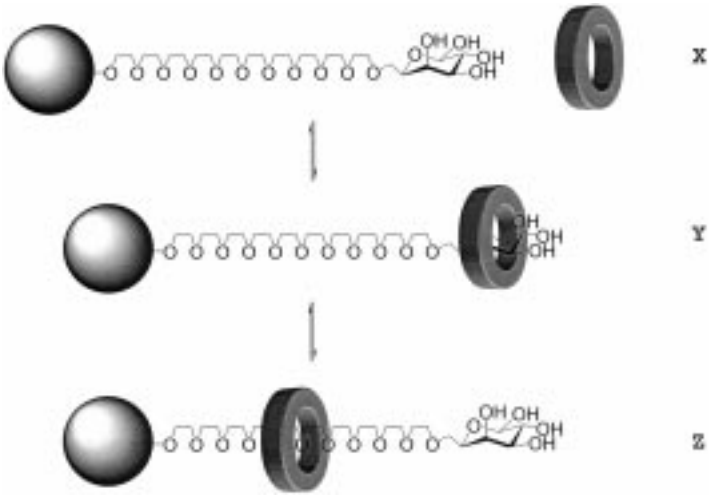


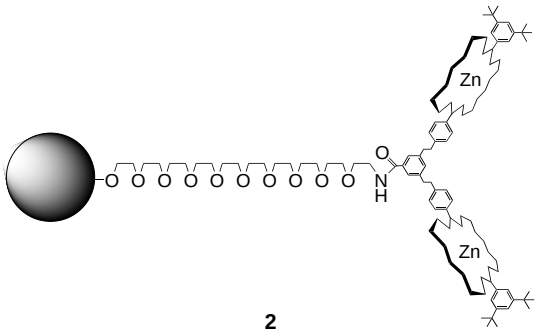
Figure 1. 400 MHz ^{1}H MAS NMR spectra of galactoside terminated beads (a) the and after addition of one equivalent of **1** (b). A splitting of the PEG resonance is observed. **X** and **Y** correspond to the combination of free PEG chain and sugar-bound macrocycle, and **Z** corresponds to the threaded macrocycle.

chain of the ArgoGel, thus resulting in threading (Scheme 1). Harada and co-workers[4] and Wenz and Keller[5] have observed a similar threading of α-cyclodextrin onto PEG chains. However, another possibility was that **1** might bind to the side of the PEG chain, with the ring current from **1** thus causing an upfield shift of the PEG resonance.

Three control experiments were carried out to explore the possibility of threading: 1) Porphyrin-terminated ArgoGel beads **2** were titrated with **1**, and showed no significant changes in the PEG resonance. This result suggests both that the porphyrin dimer attached to the end of the PEG chain acts as a stopper, thus preventing **1** from threading, and that **1** does not bind to the PEG chain on the side. 2) Unfunctionalized ArgoGel-Cl beads were titrated with **1**, and gave a broadened and upfield-shifted ($\Delta\delta = 0.6$ ppm) PEG resonance. Upon addition of glucoside, the resonance for the PEG chain sharpened and shifted towards the original chemical shift.



Scheme 1. Proposed binding modes of receptor **1** to galactosyl beads.



2

These observations indicate that **1** was threaded around the PEG chain in the first instance which caused a broadening and a change in the chemical shift. This effect was then reversed by the addition of octyl glucopyranoside. Since **1** is known to be a good receptor for sugars, the presence of glucoside causes **1** to dethread from the PEG chain, so that the broadened and upfield-shifted PEG resonance moved downfield and sharpened (Figure 2). 3) An NMR titration between hexaethylene glycol and **1** was carried out in solution, and a binding constant of approximately 9000 M^{-1} was observed. This value indicates that polyethylene glycol does bind to **1**. The NOESY spectrum of the 1:1 mixture of **1** and galactosyl beads showed NOE cross-peaks between the galactosyl proton and the aromatic protons of **1**. These experiments suggested that the three proposed modes **X**, **Y**, and **Z** in Scheme 1 do co-exist. The splitting of the PEG resonance shown in Figure 1b might arise from slow exchange between the bound, unbound, and threaded macrocycle, or from some of the PEG chains being inaccessible as a result of cross-linking, a process that might occur during chemical modification.

To further support our interpretation and demonstrate the analytical power of gel-phase MAS NMR we prepared the porphyrin-stoppered rotaxane **3** as shown in Scheme 2. The ^{1}H MAS NMR spectrum showed resonances of porphyrin dimer and **1**, but most importantly the splitting of the PEG resonance was once again observed. The outer aromatic protons of **1** were now inequivalent as a result of the large ring current of the porphyrin stopper making one side of the

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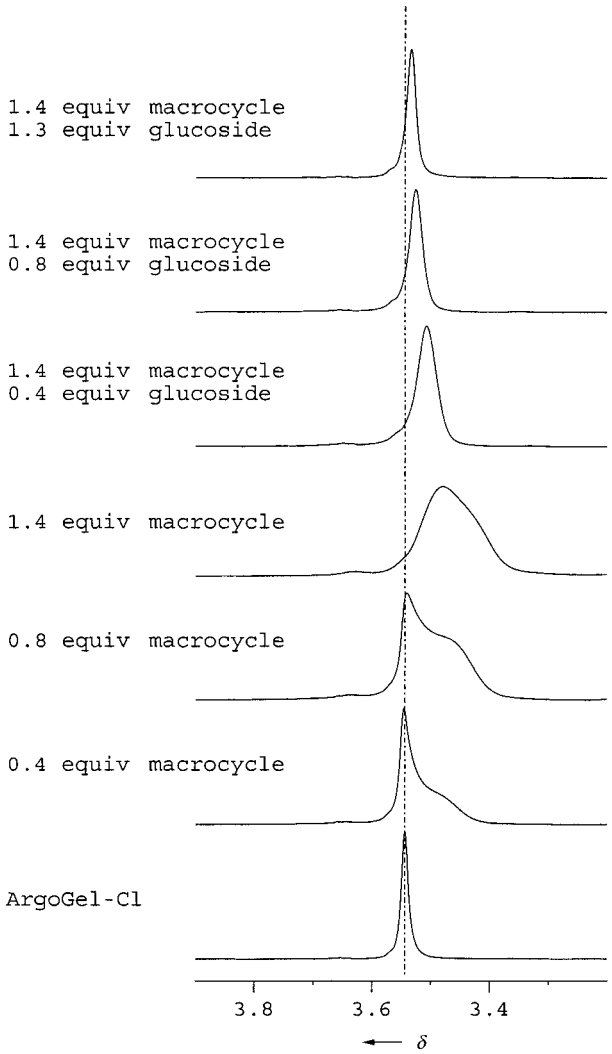
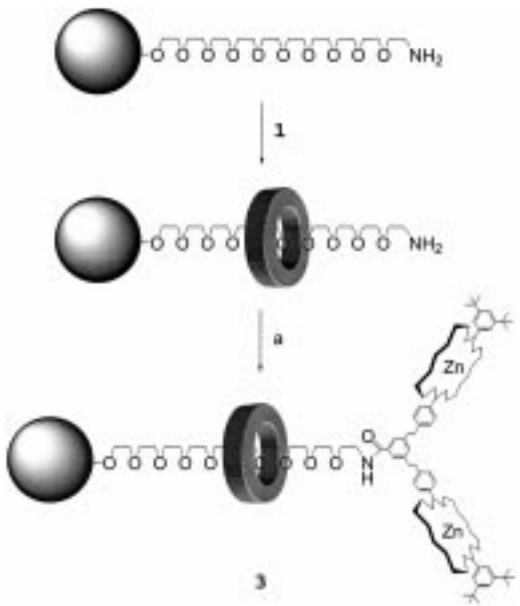


Figure 2. Control experiment showing the competition between the PEG chain of ArgoGel and octyl glucopyranoside for macrocycle **1**.



Scheme 2. Synthesis of porphyrin-stoppered rotaxane. a) Porphyrin dimer, TBTU, and $(i\text{Pr})_2$NH in chloroform.

macrocycle different from the other. The COSY MAS NMR spectrum allowed assignment of the pentyl side chains of **1** and the NOESY spectrum gave NOE cross-peaks between the PEG chain and the aromatic protons of **1** and between the PEG chains and the pentyl groups of **1** (Figure 3). Since the beads were extensively washed with chloroform and methanol, no free macrocycle should be trapped inside the beads. In any case, we would not expect to detect NOEs between the PEG chains and the free macrocycle. We conclude that **1** is held on the PEG chain as a rotaxane and stoppered by the porphyrin dimer.

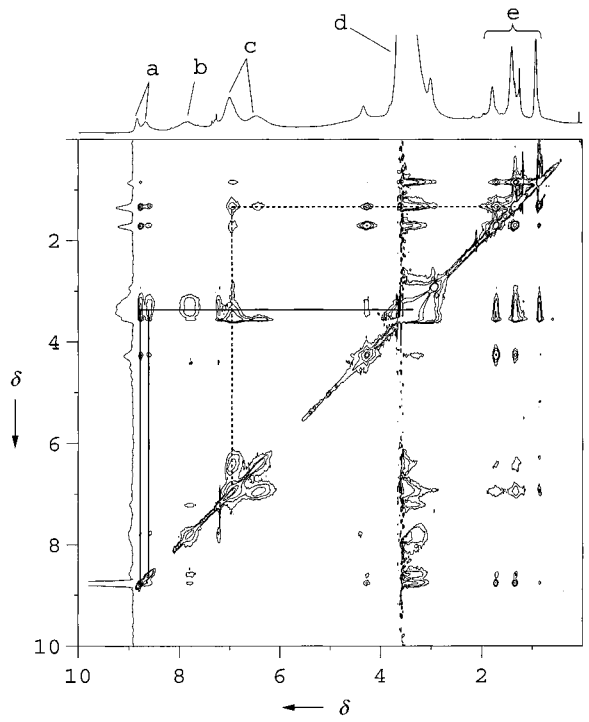


Figure 3. NOESY MAS NMR spectrum of porphyrin-stoppered rotaxane **3** showing NOE cross-peaks between the PEG chain and the outer aromatic protons of **1** (solid line), and between the polystyrene backbone of the ArgoGel and the pentyl side chain of **1** (dotted line). The 1D spectrum shown on the F2 axis is the ^{1}H MAS NMR spectrum of **3**, and the 1D spectrum shown inside the box is a cross-section taken from the NOESY experiment at $\delta = 8.87$. Resonances a correspond to the inequivalent outer aromatic protons of **1** (see text), and resonances b, c, d, and e correspond to the other aromatic protons of **1**, the polystyrene backbone of ArgoGel, PEG, and the pentyl side chains of **1**, respectively.

In conclusion, we have successfully used MAS NMR spectroscopy to confirm the possibility of a tricyclic polyamide receptor threading around the PEG chain of ArgoGel. This observation has led us to the synthesis of a solid-supported rotaxane. Further study, using different macrocycles and stoppers, is currently underway.

Experimental Section

NMR spectra were acquired at room temperature on a Bruker DRX400 spectrometer using a Bruker HR MAS probe. Rotors containing a suspension of the beads in a mixture of $CDCl_3$ and CD_3OD (92:8) were spun at 4 kHz. One-dimensional spectra were obtained using 64 scans and titrations were carried out using 10 μL injections of **1** (ca. 0.2 equiv). NOESY MAS NMR spectra were obtained at room temperature with

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suppression at the PEG resonance (70 dB), a 200 ms mixing time, 32 scans, and 512 increments.

The solution-state NMR titration between hexaethylene glycol and **1** was carried out at room temperature by monitoring the inner aromatic proton of the spacer unit. The results showed that the stoichiometry corresponds approximately to a 1:1 binding model.

Galactosyl beads: 1,2:3,4-Di-*O*-isopropylidene-D-galactopyranose (ca. 50 equiv with respect to the loading of Argogel-Cl) was treated with sodium hydride (ca. 100 equiv) in tetrahydrofuran. After filtration of the mixture, the filtrate was added to ArgoGel-Cl ($0.41-0.45\ mmol\,g^{-1}$) and shaken for 2 days. The resulting beads were washed and deprotected with a mixture of trifluoroacetic acid and water (9:1, 2 mL). Washing the beads with tetrahydrofuran, methanol, and chloroform afforded the galactosyl beads.

2: A solution of a rigid porphyrin dimer[6] (50 mg) and palladium on carbon (50 mg) in tetrahydrofuran (25 mL) was stirred under hydrogen for 24 h. Filtration of the mixture through celite and removal of the solvent afforded a flexible porphyrin dimer. A mixture of ArgoGel-NH_2 (13 mg, $0.41-0.45\ mmol\,g^{-1}$), flexible porphyrin dimer (30 mg), TBTU (4 mg), and diisopropylamine (3 mg) in a mixture of *N*,*N*-dimethylformamide (1 mL) and dichloromethane (0.5 mL) was shaken for 4 days. The solvent was then removed by filtration and the beads were washed extensively with dichloromethane and methanol.

3: A mixture of the flexible porphyrin dimer (22 mg), TBTU (5 mg), and diisopropylamine (3 mg) in chloroform (1 mL) was added to a mixture of **1** (12 mg) and ArgoGel-NH_2 (15 mg) in chloroform (1 mL). The resulting mixture was shaken for 1 day. The solvent was then removed by filtration and the beads were washed extensively with dichloromethane and methanol.

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Cobalt(II)-Nitronyl Nitroxide Chains as Molecular Magnetic Nanowires**

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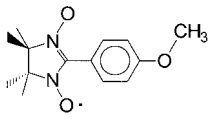
The observation of slow magnetic relaxation in molecular clusters is now considered as one of the most important achievements of molecular magnetism of the last few years.[1] In fact systems like Mn12, Fe8 have provided unique opportunities for the investigation of molecular magnetic hysteresis,[2] quantum tunneling of the magnetization,[3, 4] and of phase interference (Berry phase).[5] All these features depend on slow magnetic relaxation.

While clusters can be considered as zero-dimensional materials, in principle slow relaxation of the magnetization can also be expected in one-dimensional (1D) materials, as suggested by Glauber in 1963.[6] However, to date, it has not been possible to observe this behavior because no suitable experimental system has been produced. In fact the conditions to be met to observe slow magnetic relaxation in 1D materials are rather stringent: 1) the ratio of the interaction within the chain, J, and that between chains, J', must be rather high, larger than 10^4; 2) the material must behave as a 1D Ising ferro- or ferrimagnet.

We have now found that slow relaxation of the magnetization and hysteresis effects which are not associated with three-dimensional (3D) order can be observed in $[Co(hfac)_2(NITPhOMe)]$ (**1**; hfac = hexafluoroacetylacetonate, NITPhOMe = 4′-methoxy-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide). We want to show that these findings provide an experimental confirmation of Glauber's prediction.



NITPhOMe

Complex **1** consists of alternating $Co(hfac)_2$ and radical moieties arranged in 1D arrays with a helical structure arising from the trigonal crystallographic

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