Templated Conversion of a Crown Ether-Containing Macrobicycle into [2]Rotaxanes

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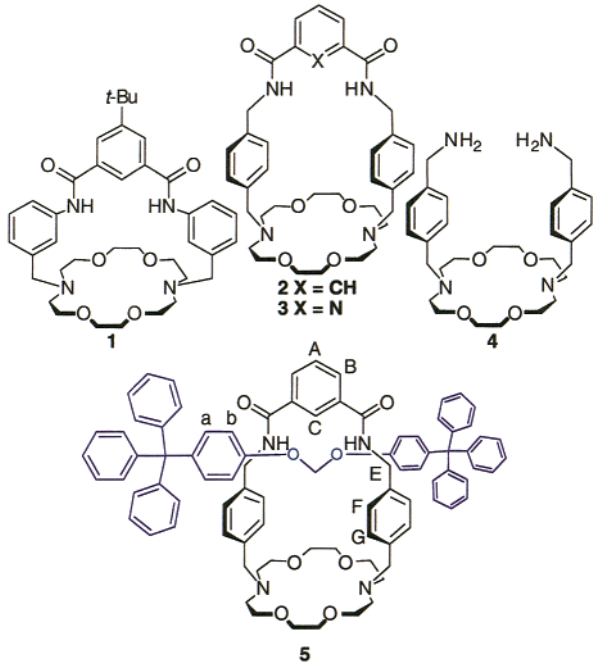
A crown ether-containing macrobicycle was used as the wheel component in a templated synthesis of a [2]rotaxane with an acetal-containing axle. The molecular structures of the macrobicycle and the [2]rotaxane were characterized by NMR spectroscopy and X-ray crystallography. The chloride-binding ability of the macrobicycle, either free in solution or when it is part of a [2]rotaxane, is quite weak as determined by NMR titration experiments. A second analogous [2]rotaxane, with a longer axle, was synthesized, and its solvent-dependent co-conformation was characterized by 2D NMR spectroscopy. The position of the wheel along the axle can be controlled by the solvent polarity, however, attempts to use metal cations such as Na^+, K^+, Ba^{2+}, and Ag^+ to switch the wheel position in polar solvents were unsuccessful.

Introduction

The field of mechanically interlocked molecules continues to grow as researchers design, synthesize, and characterize increasingly complicated structures.[1] Our research group is interested in preparing [2]rotaxanes, interlocked molecules that comprise two components, a wheel and a penetrating axle. More specifically, we are investigating [2]rotaxanes with salt-binding wheels,[2] with the eventual goal of making molecular devices with salt-dependent properties. Recently, we reported that macrobicycle **1** (Scheme 1) is able to extract and bind alkali halide salts as their contact ion pairs.[3] Molecular models of **1** indicate that its cavity is not large enough to accommodate a penetrating axle. Therefore, we designed the larger macrobicycles **2** and **3** with the idea that they could be converted into novel benzyl amide [2]rotaxanes.[4] Here, we describe the synthesis and structural characterization of **2** and **3** and demonstrate how **2** can be used to make [2]rotaxanes with acetal-linked axles. We also provide a comparison of the chloride-binding ability of **2** when it is the free macrobicycle to that when it is part of a [2]rotaxane. Finally, we evaluate the ability of a [2]-rotaxane analogue with a long axle to act as a molecular shuttle.

Scheme 1



Results and Discussion

Macrocycle Synthesis and Structure. Macrobicycles **2** and **3** were prepared in yields of 45 and 15%, respectively, by reacting the known diamine **4**[5] with isophthaloyl dichloride or 2,6-pyridine di(carbonyl chloride), respectively. The ^{1}H NMR spectrum of **2** in $CDCl_3$ contains broad lines, indicating slow conformational

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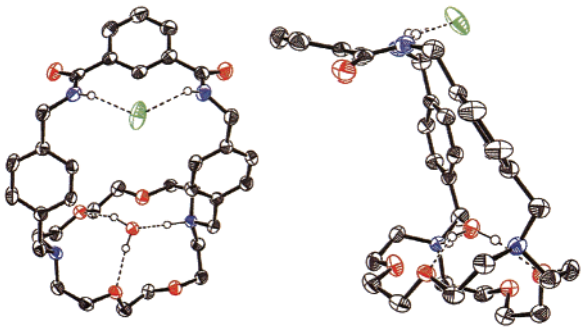
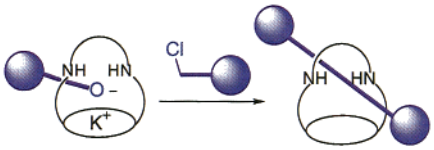


Figure 1. Two views of the X-ray crystal structure of **2**·HCl·H_2O. Only relevant hydrogen atoms are shown, and the second water is omitted for clarity. Structure shows 50% ellipsoid probability.

Scheme 2



exchange, whereas the $CDCl_3$ spectrum of **3** is more resolved, suggesting that **3** is more rigid. This rigidity is probably related to the ability of the pyridyl nitrogen in **3** to form internal hydrogen bonds with the adjacent NH residues.[4−6] The HCl salt of **2** is also soluble in organic solvents, and its structure was characterized by mass spectrometry, NMR spectroscopy, and X-ray crystallography. Two views of the X-ray crystal structure of the **2**·HCl salt are shown in Figure 1. The plane of the bridging isophthalamide unit is almost parallel to the plane of the diazacrown ring, and the Cl^- is hydrogen-bonded to the two NH residues on the exo face of the macrocyclic cavity (N−Cl = 3.27 Å). One of the crown nitrogen atoms is protonated and hydrogen-bonded to a water molecule that is bound deeply within the cavity (N−OH_2 = 2.80 Å). The electron density is sufficiently defined to show that the structure is not a bound H_3O^+ inside the free base of **2**.

Rotaxane Synthesis and Structure. [2]Rotaxane **5** was prepared by the anion template method.[2,7] The free base of macrobicycle **2** was treated with 2 molar equiv of potassium 4-tritylphenolate in methylene chloride. The tritylphenolate presumably reacts with the methylene chloride to form a chloromethyl ether,[8] which then reacts in situ with a second potassium tritylphenolate inside the cavity of **2** to give **5** in 15% yield (Scheme 2). Surprisingly, attempts to convert **3** into an analogue of **5** were unsuccessful; only the unthreaded free axle was isolated. There appear to be two possible reasons for this outcome: (a) repulsion between the pyridyl nitrogen and the phenolate oxygen may preclude wheel threading or (b) the wheel-threading step may require a flexible macrocycle cavity space that can accommodate the reacting partners and the changing geometry of the nucleophilic substitution reaction. Macrocbicycle **3** may be unable to do this step because it has a more rigid structure and a less accessible cavity.

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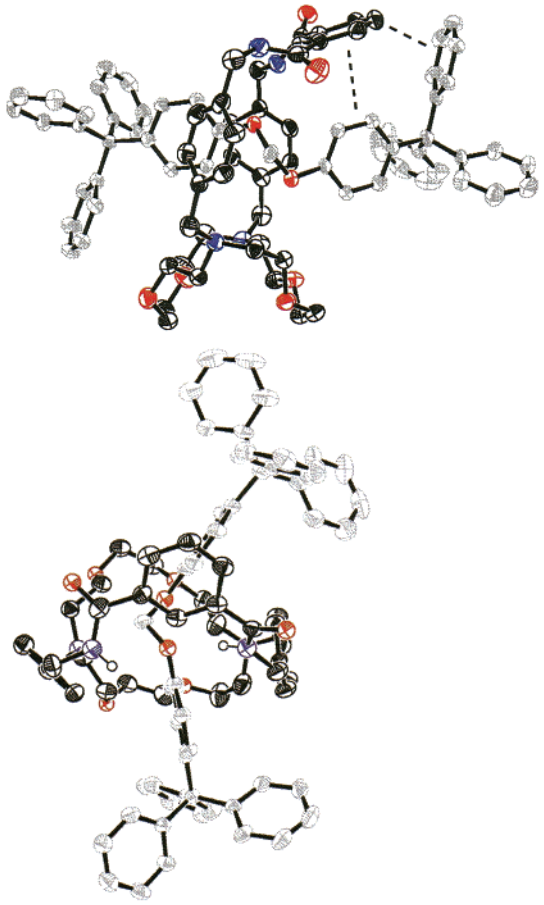


Figure 2. Two views of the X-ray crystal structure of **5**. Axle carbons are shown in gray for clarity. Prominent aromatic edge-to-face interactions are indicated with dashed lines. Amide hydrogens are shown in the second view; all other hydrogens and three waters are omitted for clarity. Structure shows 50% ellipsoid probability.

A sample of **5** was crystallized, and its structure was determined by X-ray diffraction (Figure 2). The X-ray structure shows a number of notable features: (1) There is apparently a long, weak hydrogen bond between one of the acetal oxygens and one of the wheel NH groups (N−O = 3.95 Å), while the other acetal oxygen contacts a crown CH residue (C−O = 3.11 Å). (2) There are a number of aromatic stacking interactions, particularly edge-to-face, between the wheel and the axle aromatic groups. (3) One of the crown nitrogen atoms points a lone pair into the macrobicyclic cavity, whereas the other points its lone pair out. (4) One of the acetal CH bonds is directed toward the crown nitrogen (C−N = 3.65 Å) and its adjacent aromatic group (CH−*p* interaction).

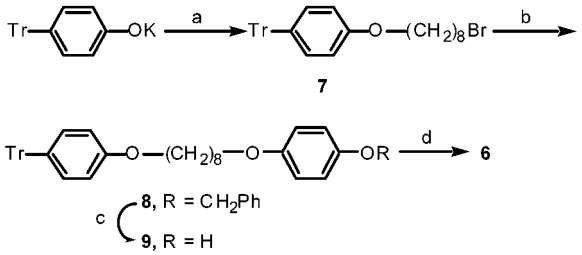
The X-ray structure of **5** helps rationalize many of its solution-state NMR spectral features. For example, the axle's central acetal protons in **5** are located between the wheel's two aromatic side-units, which explains why the acetal chemical shift is significantly upfield (4.17 ppm in $CDCl_3$) compared to that of the free axle (5.69 ppm). Signals for the wheel aromatic protons F and G and axle aromatic protons a and b are shielded because of aromatic stacking. The structure of **5** appears to be fairly rigid because even at −60 °C the ^1H NMR in $CDCl_3$ shows no signal splitting due to slow conformational exchange. In addition, a ^1H spectrum in DMSO-d_6 shows sharp signals,

Table 1. Chloride Association Constants, K_{Cl^-} (M^{-1}), for Receptors 1, 2, and 5 in the Presence or Absence of 1 Molar Equivalent of Metal Tetraphenylborate[a]

receptor	K_{Cl^-}	receptor	K_{Cl^-}
1	35[b]	**2**	5
1 + Na^+	50[b]	**2** + Na^+	5
1 + K^+	460[b]	**2** + K^+	15
5	2	**5** + Na^+	2
5 + K^+	5		

[a] In DMSO-d_6 at T = 295 K; initial [receptor] = 10 mM; uncertainty ±15%. [b] From ref 3.

Scheme 3[a]



[a] Key: (a) 1,8-dibromooctane, KI (cat.), CH_3CN, reflux, 18 h, 53%; (b) 4-benzyloxyphenol, KI (cat.), K_2CO_3, CH_3CN, reflux, 24 h, 66%; (c) H_2, Pd/C, MeOH/THF 1:1, 3 h, 88%; (d) **2**, K_2CO_3, CH_2Cl_2, 24 h, 14%.

which is in contrast with our previously reported [2]-rotaxane system.[2]

Chloride-Binding Abilities. The chloride-binding properties of macrobicycle **2** and [2]rotaxane **5** were evaluated in the following way. Receptor/Cl^- association constants in highly polar DMSO-d_6 were determined by adding aliquots of tetrabutylammonium chloride to a solution of receptor **2** or **5** in the absence or presence of 1 molar equiv of potassium or sodium tetraphenylborate. The diffuse tetrabutylammonium cation and tetraphenylborate anion have negligible affinity for the receptors, thus they are simply "spectator ions". The complex-induced changes in chemical shift are consistent with the Cl^- forming hydrogen bonds with the isophthalamide NH residues, and association constants were obtained by fitting the titration isotherms to a 1:1 binding model using an iterative computer method.[9] As shown in Table 1, the benzyl amides **2** and **5** have similar and significantly weaker affinities for Cl^- than does the more acidic aromatic amide **1**. In addition, their Cl^- association constants are not affected by the presence of Na^+ and increase by a factor of 2−3 only in the presence of K^+. This modest binding enhancement is most likely attributable to the relatively large distance between the anion and cation binding sites in **2** and **5**.

Evaluation of a Potential Molecular Shuttle. To demonstrate further the utility of **2** as a wheel component, we used the same anion template method (Schemes 2 and 3) to prepare [2]rotaxane **6** (Figure 3) in 16% yield. [2]Rotaxane **6** has a longer acetal-containing axle, and a battery of NMR methods (COSY, HETCOR, TOCSY, ROESY) were used to characterize its co-conformation in $CDCl_3$ (Table 2) and DMSO-d_6. In both solvents, the peaks are sharp at room temperature. The chemical shift of the acetal signal is hardly changed compared to that of the free axle, and the acetal protons do not cross-relax any wheel protons, suggesting that the acetal linkage is

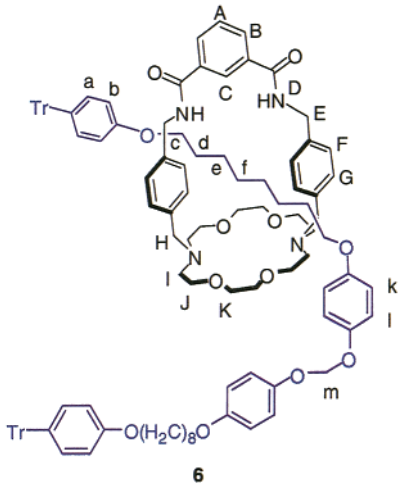


Figure 3. [2]Rotaxane, **6**, shown with protons labeled (Tr = $C(Ph)_3$).

Table 2. Proton Assignments for Rotaxane, 6, in $CDCl_3$

proton	δ (ppm)	proton	δ (ppm)
A	7.59	a	7.10
B	8.22	b	6.66
C	8.19	c	3.54
D	6.91	d	1.52
E	4.43	e	1.22
F	6.88	f	1.19
G	6.93	g	1.19
H	3.48, 3.47	h	1.27
I	2.67, 2.74	i	1.57
J	3.60, 3.62	j	3.64
K	3.59	k	6.73
		l	6.96
		m	5.54

not inside the wheel. In $CDCl_3$, it appears that the wheel spends most of its time over the phenoxy rings attached to the axle-stoppers. In particular, a ROESY spectrum shows a cross-peak between wheel proton C and the shielded aromatic axle protons b. Presumably, this preferred co-conformation is stabilized by aromatic stacking interactions that are similar to those seen in Figure 2. The symmetrical simplicity of the ^1H NMR spectrum of **6** in $CDCl_3$ indicates that the spinning of the wheel and the shuttling of the wheel along the axle are both very rapid, even at −60 °C.

A ROESY spectrum in DMSO-d_6 shows no cross-peaks between wheel proton C and any axle aromatic protons, but cross-peaks are observed with the axle alkyl protons, suggesting that the wheel resides on one of the two alkyl chains. This result is reminiscent of the solvophobic effect previously reported by Leigh and co-workers.[10] The rotaxane adopts a co-conformation that reduces exposure of the lipophilic alkyl chains to the polar solvent and increases exposure of the relatively more polar phenoxy rings attached to the axle-stoppers. This solvophobic effect is apparently stronger than any available aromatic stacking effect. Attempts to use metal cations to induce the wheel in [2]rotaxane **6** to reside over the central acetal linkage were unsuccessful. Addition of excess Na^+, K^+, Ba^{2+}, or Ag^+ perchlorate salts to solutions of **6** in DMSO-d_6 does not induce any significant change in the chemical shift of the axle acetal protons. The NMR

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signals for the crown protons do change appreciably, however, indicating that the metal cations do bind to the rotaxane.

Summary

We have shown how crown ether-containing macrobicycle **2** can be used to make novel benzyl amide [2]-rotaxanes **5** and **6** with acetal-containing axles. The co-conformation of **6** is quite sensitive to solvent polarity; however, unlike our previously reported example,[2] the co-conformation is apparently not affected by the presence of metal cations. Further studies of this class of [2]-rotaxanes as potential molecular devices such as shuttles and triggered release agents will be reported in due course.

Experimental Section

Macrobicycle 2. Diamine **4**[5] (0.430 g, 0.86 mmol) was dissolved in THF (250 mL). Separately, 5-(*tert*-butyl)isophthaloyl dichloride (0.174 g, 0.86 mmol) was dissolved in the same volume of THF. A 1 L three-neck, round-bottom flask was charged with 100 mL of THF and triethylamine (260 μL, 1.89 mmol). Via two pressure-equalizing dropping funnels, both reactants were added simultaneously dropwise to the flask with vigorous stirring under nitrogen at ambient temperature. The cloudy solution was stirred for 24 h, and the solvent was removed under vacuum, leaving a yellow gossamer. The crude material was dissolved in CH_2Cl_2 and washed successively with saturated $NaHCO_3$ and deionized water. Evaporation of the organic layer and purification on a silica column (90:10 CH_2Cl_2/MeOH, then MeOH eluent) yielded pure **2** (0.245 g, 45%); mp 99−101°; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.92 (t, 2H, J = 5.4 Hz), 8.28 (s, 1H), 7.95 (d, 1H, J = 7.8 Hz), 7.59 (t, 2H, J = 7.8 Hz), 7.28 (AB q, 8H, J = 8.1 Hz), 4.48 (d, 4H, J = 5.7 Hz), 3.58 (s, 4H), 3.50 (t, 8H, J = 5.4 Hz), 3.49 (s, 8H), 2.60 (t, 8H, J = 5.4 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.1, 138.7, 136.7, 135.1, 131.0, 129.6, 129.5, 128.1, 124.3, 70.9, 70.1, 59.7, 53.9, 44.1. HRMS (FAB$^+$, [M + H]$^+$) calcd for $C_{36}H_{46}N_4O_6$ 631.3496, found 631.3507 m/z.

2·HCl: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, 2H, J = 8.0 Hz), 7.86 (s, 1H), 7.40 (t, 1H, J = 8.0 Hz), 7.20 (AB q, 8H, J = 8.0 Hz), 6.70 (t, br, 2H, J = 5.4 Hz), 4.47 (d, 4H, J = 5.5 Hz), 3.65 (s, 4H), 3.60 (m, 16H), 2.67 (t, 8H, J = 5.5 Hz). MS (FAB, [M + H + HCl]$^+$) 667 m/z. Crystal data for **2**·HCl: $C_{36}H_{47}ClN_4O_6$, monoclinic, $P(2)1/n$, a = 12.378(2) Å, b = 18.341(3) Å, c = 17.614(3) Å, α = 90°, β = 102.507(5)°, γ = 90°, V = 3904.2(11) Å^3, Z = 4, T = 170(2) K, μ(Mo Kα) = 0.156 mm^{-1}, D_{calcd} = 1.275 mg/m^3, R1 ($I > 2\theta(I)$) = 5.27%, wR2 ($I > 2\theta(I)$) = 8.84% for 5598 observed independent reflections. The X-ray data for **2**·HCl can be retrieved from the Cambridge Crystallographic Data Center using deposition number CCDC 171662. Crystals were obtained by slow evaporation from ethanol.

3. The pyridyl macrobicycle **3** was prepared following the same synthetic procedures for **2** and obtained in 15% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, 2H, J = 7.8 Hz), 8.11 (t, br, 2H), 8.02 (t, 1H, J = 7.7 Hz), 7.41 (d, 4H, J = 8.1 Hz), 7.27 (d, 4H, J = 8.1 Hz), 4.60 (d, 4H, J = 5.7 Hz), 3.75 (bs, 4H), 3.68 (t, 8H, J = 5.4 Hz), 3.64 (s, 8H), 2.76 (t, 8H, J = 5.4 Hz) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 148.9, 139.2, 136.6, 129.6, 128.1, 125.2, 125.0, 71.1, 69.9, 59.8, 54.4, 43.5 ppm. HRMS (FAB$^+$, [M + H]$^+$) calcd for $C_{35}H_{45}N_4O_6$ 632.3448, found 632.3445 m/z.

5. Macrobicycle **2** (0.037 g, 0.06 mmol) and potassium 4-tritylphenolate (0.045 g, 0.12 mmol, 2.0 equiv) were dissolved in freshly distilled CH_2Cl_2 (5 mL) with stirring under nitrogen at ambient temperature. Stirring was continued for 24 h, at which time the solvent was removed by rotary evaporation. The crude material was purified on a silica column by elution with CH_2Cl_2 to remove the axle and unreacted phenol, followed by 95:5 CH_2Cl_2/MeOH to obtain the desired rotaxane **5** (0.012 g, 15%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, 2H, J = 8.0 Hz), 8.00 (s, 1H), 7.43 (t, 1H, J = 8.0 Hz), 7.29−7.19 (m, 30H), 7.04 (d, 4H, J = 9.0 Hz), 6.71 (AB q, 8H, J = 8.0 Hz), 6.66 (t, 2H, J = 5.0 Hz), 6.24 (d, 4H, J = 9.0 Hz), 4.38 (d, 4H, J = 4.5 Hz), 4.17 (s, 2H), 3.51 (s, 4H), 3.43 (t, 8H, J = 5.5 Hz), 3.33 (s, br, 4H), 3.17 (s, br, 4H), 2.70 (s, br, 4H), 2.62 (s, br, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 153.4, 147.0, 141.3, 137.2, 136.2, 134.5, 132.6, 131.8, 131.2, 129.9, 129.4, 128.6, 127.9, 126.2, 123.5, 114.3, 70.7, 70.1, 64.6, 59.7, 52.3, 44.6. MS (FAB$^+$, [M + H]$^+$) calcd for $C_{87}H_{86}N_4O_8$ 1314.64, found 1314.52 m/z. X-ray data for 5: $C_{87}H_{86}N_4O_8$, triclinic, $P\bar{1}$, a = 12.784(3) Å, b = 15.522(3) Å, c = 19.931(4) Å, α = 90.145(4)°, β = 104.412-(4)°, γ = 93.480(4)°, V = 3823.0(13) Å^3, Z = 2, T = 170(2) K, μ(Mo Kα) = 0.078 mm^{-1}, D_{calcd} = 1.190 mg/m^3, R1 ($I > 2\theta(I)$) = 7.23%, wR2 ($I > 2\theta(I)$) = 18.41% for 10968 observed independent reflections (4° = 2θ = 46°). The X-ray data for **5** can be retrieved from the Cambridge Crystallographic Data Center using deposition number CCDC 171663. Crystals were grown by slow evaporation from ethanol.

6. K_2CO_3 (0.019 g) was added to a solution of macrobicycle **2** (0.022 g, 0.034 mmol) and phenol **9** (0.038 g, 0.069 mmol) in freshly distilled CH_2Cl_2 (5 mL), and the mixture was stirred for 3 days. After removal of the solvent, the residue was purified on a silica column by elution with CH_2Cl_2 to remove the axle and unreacted phenol, followed by 95:5 CH_2Cl_2/MeOH to obtain the desired rotaxane **6** (0.010 g, 16%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, 1H, J = 1.2 Hz), 8.22 (d, 1H, J = 1.2 Hz), 8.20 (s, 1H), 7.60 (t, 1H, J = 7.8 Hz), 7.26−7.17 (m, 34H), 7.10 (d, 4H, J = 5.4 Hz), 6.96−6.95 (m, 8H), 6.90 (t, 2H, J = 4.8 Hz), 6.88 (d, 4H, J = 7.8 Hz), 6.74 (d, 4H J = 9.0 Hz), 6.66 (d, 4H, J = 6.7 Hz), 5.47 (s, 2H), 4.45 (d, 4H), 3.64−3.47 (m, 28H), 2.74 (s, br, 4H), 2.67 (s, br, 4H), 1.60−1.54 (m, 8H), 1.19−1.28 (m, 16H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 156.7, 154.4, 151.0, 147.2, 139.3, 137.2, 135.8, 134.1, 132.4, 132.3, 132.2, 131.3, 131.2, 130.0, 129.8, 128.5, 127.6, 127.5, 126.1, 126.0, 123.1, 117.9, 115.4, 113.3, 92.9, 70.9, 70.1, 68.6, 68.0, 64.5, 62.1, 59.5, 52.4, 44.7, 29.5, 29.4, 29.3, 27.7, 26.1. MS (ESI, [M + H]$^+$) calcd for $C_{115}H_{126}N_{54}O_{12}$ 1757.26, found 1757.52.

7. Potassium 4-tritylphenolate (0.2 g, 0.53 mmol), 1,8-dibromooctane (0.14 g, 0.53 mmol), and a catalytic amount of KI (0.010 g, 0.084 mmol) were dissolved in acetonitrile (30 mL) and refluxed for 18 h. Evaporation of the solvent gave the crude product, which was purified by chromatography (SiO_2; hexane/CH_2Cl_2; 70:30) to afford a white solid (0.15 g, 53%); mp 133−137°; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32−7.20 (m, 15H), 7.15 (d, 2H, J = 9 Hz), 6.79 (d, 2H, J = 9 Hz), 3.96 (t, 2H, J = 6.9 Hz), 3.44 (t, 2H, J = 6.9 Hz), 1.92−1.88 (m, 2H), 1.83−1.75 (m, 2H), 1.53−1.48 (m, 4H), 1.46−1.40 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.2, 147.2, 138.9, 132.3, 131.3, 127.5, 126.0, 113.3, 67.9, 64.4, 34.1, 32.9, 29.4, 29.3, 28.8, 28.7, 28.2, 26.1. HRMS (FAB$^+$, [M + H]$^+$) calcd for $C_{33}H_{35}BrO$ 526.1871, found 526.1864.

8. A solution of **7** (0.15 g, 0.28 mmol), 4-bezyloxyphenol (0.056 g, 0.28 mmol), potassium carbonate (0.039 g, 0.028 mmol) and catalytic amount of KI (0.010 g, 0.084 mmol) were refluxed in acetonitrile (30 mL) for 24 h. The solvent was removed in vaccuo and the residue chromatographed (SiO_2; hexane:CH_2Cl_2; 70:30). A white solid was obtained after removal of the solvents (0.12 g, 66%); mp 131−133°; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.31 (m, 5H), 7.32−7.20 (m, 15H), 7.16 (d, 2H, J = 9 Hz), 6.93 (d, 2H, J = 9 Hz), 6.93−6.80 (m, 4H), 5.05 (s, 2H), 3.97−3.94 (m, 4H), 1.88−1.78 (m, 4H), 1.58−1.40 (m, 8H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.2, 153.7, 153.0, 147.2, 138.9, 137.5, 132.3, 131.3, 128.7, 127.6, 126.0, 116.0, 115.5, 113.4, 70.9, 68.7, 68.0, 64.5, 29.6, 29.5, 26.2, 26.1. HRMS (FAB$^+$, [M + H]$^+$) calcd for $C_{46}H_{46}O_3$ 646.3447, found 646.3437.

9. Compound **8** (0.100 g, 0.006 mmol) was dissolved in methanol/THF (1:1) (30 mL) and a catalytic amount (0.030 g) of Pd/C (10% w/w) was added and stirred under H_2 at room temperature for 3 h. After complete reaction the solution was filtered and the solvent removed using a rotary evaporator to give **9** (0.075 g, 88%) as a white solid; mp 80−83°; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32−7.20 (m, 15H), 7.11 (d, 2H, J = 9 Hz), 6.81−6.76 (m, 6H), 3.94−3.90 (m, 4H), 1.79−1.77 (m, 4H), 1.47−1.40 (m, 4H), 1.40 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ

157.2, 153.4, 149.6, 147.2, 138.9, 132.3, 131.3, 127.6, 126.0, 125.7, 116.2, 115.8, 113.4, 68.8, 68.0, 64.5, 30.5, 29.5, 29.4, 26.2, 26.1. HRMS (FAB^+, $[M + H]^+$) calcd for $C_{39}H_{40}O_3$ 556.2977, found 556.2962.

^{1}H NMR Titrations. All salts and NMR solvents were purchased from Aldrich and, after being checked for purity, were used as supplied. $K(BPh)_4$ was synthesized according to a literature procedure.[11] The receptor was titrated with tetrabutylammonium chloride in the presence and absence of alkali tetraphenylborate. In each case, a 10 mM solution of the receptor in DMSO-d_6 was prepared in a 5 mm NMR tube (solution volume 750 μL). Where applicable, the solution also contained 1 molar equiv of alkali tetraphenylborate. Small aliquots of tetrabutylammonium chloride stock solution (0.75 M) were added, and a spectrum was acquired after each addition. Care was taken to avoid water absorption from the atmosphere. Titration isotherms for all receptor protons that exhibited significant complexation-induced shifts were fitted to a 1:1 binding model using an iterative curve-fitting method that has been previously described.[9] For each system, the extracted association constants for the different isotherms were within 15% of the average value.

(11) Honda, H.; Ono, K.; Murakami, K. *Macromolecules* **1990**, *23*, 515−520.

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Supporting Information Available: ^{1}H NMR spectra for **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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