

Tetrahedron 56 (2000) 4501-4509

Molecular Design using Electrostatic Interactions. Part 2: Synthesis and Properties of Flexible Dipodand Di- and Tetra-cations with Restricted Conformations. Charge, Shape and Size in Molecular Complexation

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Received 21 January 2000; revised 13 March 2000; accepted 30 March 2000

Abstract—A number of dipodand dications and tetracations were synthesised with structures based on 1,2,4,5-, penta- and hexa-substituted benzene, DABCO substituents providing the positive charges. The binding of these polycations in water to a variety of polyanions was examined with respect to the effect of the 'spectator' counter cations on the observed association constants. The polycations precipitate ferriand ferrocyanide, in some cases preferentially for one oxidation state, and an X-ray crystallographic analysis of the complex between the tetracation **5** and ferricyanide reveals the complexity involved even in the molecular recognition of small, charged compounds. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

The design of systems that can recognise specific anions has been an active research area since Simmons and Park¹ in 1968 reported the encapsulation of halide ions in a charged molecular framework. A variety of polyammonium macrocycles have been subsequently prepared, which can bind anions with varying degrees of specificity²⁻⁴ with the guest anion penetrating into the cavity of the host molecule and being bound by electrostatic and specific hydrogen bond interactions.⁵⁻⁷ These studies were carried out on the protonated species under acidic conditions and in order to investigate the process over a wider pH range a variety of quartenary salts were prepared, mainly by methylation of the parent tertiary amines, and their binding affinities studied.⁸⁻¹¹ These hosts are soluble in water but guest complexion again appears to be by inclusion,¹² although the possibility of hydrogen bonding from nitrogen has been lost. A series of cyclophanes with disubstituted diazabicyclo[2.2.2]octanes [DABCO] providing the cationic charge were found to bind large anions on the outside of the cavity¹³ and, consequently, the binding constants did not vary greatly with ring size. The DABCO motif had previously been used in compounds designed as membrane transfer agents for ATP, but these suffered from the deter-

Keywords: molecular recognition; polycations; carboxylates; X-ray.

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The initial interaction of all molecules in the cell is probably electrostatic since all other types of interaction fall off much more rapidly with distance.¹⁸ Many of these biomolecules will be charged and the interaction may be with another charged molecule or with a molecule that can be polarised. In order to study simple electrostatic interactions in water, we prepared tripodand molecules based on benzene with DABCO units providing the cationic charge.¹⁹ These were shown to bind differentially to a number of anions and the hexasubstituted derivatives, where rotation is restricted, were found to have higher binding affinities than the trisubstituted analogues. The cations could, in some cases, select between ferri- and ferrocyanide anions and the role of bound water in these and related polycation complexes determined by X-ray crystallography.20 Similar systems using imidazole and pyrazole rather than DABCO, which involve both electrostatic and hydrogen bonding, have been described by others.^{21–23}

We now report the synthesis of a series of polycation hosts based on substituted benzene frameworks with DABCO substituents again providing the cationic centres. We have examined the interaction of these hosts with a variety of

gent properties which disrupted the liposome vesicles.^{14,15} The guanidinium group has also been used to provide the charge in cation hosts and both cyclic systems¹⁶ and acyclic systems¹⁷ with this function have been shown to bind significantly to phosphate ions with significant binding constants.



Scheme 1.

polyanions, altering both their shape and charge. These interacting molecules, although much smaller than their biological counterparts, must undergo the same sequence of events, coulombic attraction, rearrangement of bound, surface water and the association into a molecular complex. We attempted to exclude factors other than coulombic interactions from this association but, of necessity, the occurrence of hydrogen bonding in the water and between the water and the ions must remain.

Results and Discussion

Synthesis

The DABCO motif is a simple method of introducing a positive charge into a designed cationic host. It is readily alkylated^{24,25} and, since the two nitrogen atoms are effectively insulated from each other, double differential alkylation is readily accomplished.²⁶ The DABCO moiety can thus be used to provide one or two charges on the selected skeletal framework if this is suitably substituted. Initially, a series of bis-bromomethylbenzenes was prepared by bromomethylation of the appropriate polymethylbenzene by van der Made's method,²⁷ as shown in Scheme 1.

The bis-benzyl-DABCO derivatives 1, 2 and 3 were prepared in this way as the dibromide salts. The FAB mass spectra all showed ions corresponding to the loss of one bromide ion. The compounds had the expected ¹H and ¹³C NMR spectra except that the proton spectrum of 1 was more complex. This was thought to arise from restricted rotation and to investigate this we converted the dibromide, which was only soluble in water to any appreciable extent, to the di-hexafluorophosphate, which is soluble in dimethyl sulfoxide. In the variable temperature ¹H NMR spectrum in DMSO the benzylic protons appear as two signals at 25°C which coalesce to a singlet at 90°C with a rotational barrier of ca. 80 kJ mol⁻¹.



Since we had found previously that the preferred route to disubstituted DABCO hosts was by reaction of the alkylated DABCO derivative with the precursor host framework molecule,¹⁹ we prepared *N*-alkyl-DABCO bromides from DABCO and the required alkyl bromide and treated these with the appropriate bromomethylbenzene as shown in Scheme 2.

The tetrabromide salts of the benzene derivatives **4**, **5** and **6** were prepared in this way, utilising 2-bromopropane to alkylate DABCO. The FAB mass spectra all showed an ion corresponding to the loss of one bromide ion. The ¹H NMR spectra were in agreement with the assigned structures and the ¹³C NMR spectra showed the expected number of carbons. The ¹H NMR spectrum of **4** showed multiple signals for the methylene groups in a way similar to that of the dicationic analogue **1**. The tetracation **4** was converted to the tetra-hexafluorophosphate which dissolved in DMSO, but attempts to determine the coalescence



temperature were frustrated by decomposition of the compound at ca. 80° C.



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A related series of compounds, **7**, **8** and **9**, were synthesised from 11-*N*-DABCO-undecanethiol, prepared by alkylation of DABCO with 11-bromo-undecanethiol, and the appropriate benzyl bromide. The FAB spectra all show ions corresponding to the loss of one bromide ion and the ¹H and ¹³C NMR spectra are consistent with the assigned structures. These compounds have been used to assemble cationic monolayers on gold surfaces.²⁸



Binding studies

The association constants of these polycations with a variety of polyanion guests were determined by ¹H NMR titration studies²⁹ and the stoichiometry of association by the method of continuous variation,³⁰ as we have described previously.¹⁹ The titrations were carried out in water and, in order to investigate the importance of spectator ions on the apparent association constants, anionic salts of lithium, sodium, potassium and calcium were used. The polycations were all in the form of their bromide salts. Dication receptor 1 showed a similar association constant with the dilithium, disodium and dipotassium 1,2-benzenedicarboxylate (Table 1). This suggests that the association constants of these complexes are all similar, in agreement with the literature association constants that show only a small variation.³¹ All three combinations had 1:1 stoichiometries. Dication 2 has a lower dissociation constant with sodium 1.2-benzenedicarboxylate but the lithium and potassium salts did not have 1:1 stochiometries, as was also found for the sodium and potassium salts of dication 3. The alkali salts of 1,3-benzenedicarboxylate gave somewhat larger association constants and all had 1:1 stoichiometries. Calcium 1,3-benzenedicarboxylate was also investigated and this had a similar association constant to the alkali salts, suggesting that the calcium ion does not bind to both anionic centres of the 1,3-dicarboxylate simultaneously. We also investigated the association of 1 with disodium and calcium dipicolinate, since dipicolinic acid is a bacterial spore component responsible for the chelation of calcium.³² In this case the association constant with calcium dipicolinate (log K 1.18) was significantly smaller than with disodium dipicolinate (log K 1.66) which was similar to that for calcium 1,3-benzenedicarboxylate ($\log K$ 1.78). This difference is consistent with the much larger association constant for calcium dipicolinate $(\log K 4.61)$ than for calcium 1,3-benzenedicarboxylate $(\log K \ 0.93)^{33}$ with the polycation 1 having difficulty in competing with the calcium ion for the dipicolinate. With calcium dipicolinate, binding of the calcium ion to both anionic centres is probably facilitated by the nitrogen lone pair and the absence of the intervening proton.

Dication 1 with trisodium 1,3,5-benzenetricarboxylate and tetrasodium 1,2,4,5-benzene-tetracarboxylate showed significant changes in the NMR chemical shift but the complexes did not have 1:1 stoichiometries. Attempts to determine the association constants of the tetracations 4-6 with the tetrasodium 1,2,3,4-benzenetetracarboxylate failed, the ¹H NMR titration plot showing at first an increasing value of the change in chemical shift with increasing host–guest ration but, after a maximum value, a further increase in the host caused a decrease in the change of the chemical shift. A more complex equilibrium situation is most probably involved in these cases, possibly with 2:1 complexes at higher cation concentrations.

Selective crystallisation

Although the cations had not given large association constants with the polyanions investigated, there did appear to be some shape preference in that the 1,3-benzenedicarboxylate salts had larger association constants than CO2

	H_a H_a H_b H_a H_b H_b H_a			H_a $\overline{O}_2 C$ N CO_2
	10	11	12	13
Cation	Anion	Counter cation	Maximum Δδ, (error) Anion protons	log K
1	10	Li ⁺	$0.055 \ (\pm 0.001)^{a}$	1.69
1	10	Na^+	$0.060 (\pm 0.004)^{a}$	1.64
1	10	K^+	$0.056 (\pm 0.001)^{a}$	1.57
2	10	Na^+	$0.064 \ (\pm 0.008)^{a}$	1.34
3	10	Li ⁺	$0.041 \ (\pm 0.002)^{a}$	1.88
1	11	Li ⁺	$0.210 (\pm 0.0025)^{b}$	1.99
1	11	Na^+	$0.229 (\pm 0.001)^{b}$	1.73
1	11	K ⁺	$0.252 (\pm 0.003)^{b}$	1.83
1	11	Ca^{2+}	$0.231 (\pm 0.004)^{b}$	1.78
2	11	Li ⁺	$0.131 (\pm 0.000)^{b}$	1.95
2	11	Na ⁺	$0.133(\pm 0.000)^{b}$	1.96
2	11	K ⁺	$0.151 (\pm 0.002)^{b}$	1.82
2	11	Ca ²⁺	$0.160 (\pm 0.001)^{b}$	1.86
3	11	Li ⁺	$0.1475 (\pm 0.002)^{b}$	1.92
3	11	Na ⁺	$0.149 (\pm 0.002)^{b}$	1.92
3	11	K ⁺	$0.152 (\pm 0.006)^{b}$	1.86
3	11	Ca ²⁺	$0.160 (\pm 0.003)^{b}$	1.85
1	12	Na ⁺	0.279 (±0.001)	1.78
2	12	Na ⁺	0.139 (±0.002)	1.89
3	12	Na ⁺	0.165 (±0.001)	1.73
1	13	Na ⁺	$0.258 \ (\pm 0.003)^{a}$	1.66
1	13	Ca ²⁺	$0.076 (\pm 0.001)^{a}$	1.18

Table 1. Maximum change in chemical shift and the association constant for a series of polycation hosts and guests with varying counter cations

^a Average $\Delta \delta$ of protons H_a and H_b . ^b $\Delta \delta$ of H_2 .

their 1,2-benzendicarboxylate analogues. We therefore investigated changing the charge on the counterion while maintaining the same geometry. For this purpose we chose the octahedral ferro- $(Fe(CN)_6^{4-})$ and ferricyanide $(Fe(CN)_6^{3-})$ ions as their potassium salts. Three experiments were done, one involving ferricyanide, one ferrocyanide and the other an equimolar mixture of the two ions, each with a dilute solution of the polycation. Where precipitates occurred they usually did so immediately, but in all cases the solutions were then left to stand for some weeks after which time some of the precipitates were crystalline. The precipitates were removed and investigated by infra-red spectroscopy, the ferrocyanide ion having an absorption at ca. 2050 cm^{-1} and the ferricyanide ion at 2110 cm^{-1} . The dication 1 gave a precipitate with ferrocyanide, ferricyanide and with the mixture, whereas the dication 2 gave precipitates

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Figure 1. Partial structure of ferricyanide complex of 5, showing two tetracations and three ferricyanide ions.



Figure 2. Partial structure of ferricyanide complex of 5, showing tetracations, ferricyanide and potassium ions but omitting water molecules.

only with ferrocyanide and the mixture. While the precipitate from **1** with the mixture showed the presence of bands at 2045 and 2109 cm⁻¹, that of **2** with the mixture showed only one band at 2056 cm⁻¹. It thus appears that the dication **2** can selectively distinguish ferro- from ferricyanide. Dication **3** did not form a precipitate in any of the experiments, which suggests that either the two cationic centres cannot readily form a cavity on the same side because of coulombic and steric repulsion or that such a cavity is too small to accommodate the ion in a suitable manner. The tetracation **4** also gave a precipitate in all three cases, the precipitate from the mixture again showing IR bands for both anions. The tetracation **5** also showed precipitates in all three cases but those for the ferricyanide and mixture produced crystals, and both of the crystalline materials had only an absorption at ca 2110 cm⁻¹. The tetracation **6** did not form a precipitate with ferrocyanide but did with both ferricyanide and the mixture, both precipitates having absorptions at ca. 2110 cm⁻¹. These differences in behaviour of the three tetracations may reflect the

differences in the rotational barriers for the DABCO substituents, **4** having the most and **5** the least hindered rotation.

An X-ray crystallographic analysis of the complex between 5 and $Fe^{III}(CN)_6$ showed that it had the formula C₇₄H₁₂₈N₂₆O₁₄Fe₃K, revealing the presence of both a spectator ion, K^+ , and 14 molecules of water in the structure. There are two tetracations and three anions in the unit cell and the extra positive charge is provided by the potassium ion. The unit cell for the complex, without the water molecules, is shown in Fig. 1 and part of the crystal structure, again without water molecules, is shown in Fig. 2. Both tetracation units are in the syn conformation, one with a ferricyanide unit partially between the pendant groups while the other shares in two external ferricyanide units. Unlike the case of the tripodand trication we have described previously,¹⁹ it would appear that the tetracation 5 is unable to accommodate the ferricyanide ion in its internal cavity and, presumably, this also applies to the ferrocyanide ion where charge matching would occur. The charge in the tripodand is more dispersed, a single charge residing on each arm, and with its larger cavity the ferricyanide is probably not required to approach as close to the benzene ring as it would in the case of the tetracation 5. We were unable to resolve the 14 water molecules in this structure but the complexity of the unit cell suggests that they probably have a more intimate 'intramolecular' role than the water molecules in the tripodand structure.²⁰

Conclusions

Rather disappointingly, the association of the polycations with a range of polyanions showed very similar binding constants. This may be due to the effect of water solvating the ions and reducing the importance of charge and shape matching. The nature of the anion counter ions also had a rather small but genuine effect on the observed association constant and such an effect is likely to be significantly larger in organic solvents. The largest effect of the counter ion was found with the dipicolinate anion, where the calcium salt is much less readily complexed than the sodium salt, which reflects the high association constant of calcium dipicolinate. Dication 1 is not, unfortunately, a superior co-ordinator of the calcium salt. Although examples of charge matched ions can be found that lead to precipitation of the host-guest complex, for example 2 with ferrocyanide, the situation with these small polycations is complex, with water and spectator ions probably playing a role in both recognition and the subsequent processes of aggregation, precipitation and crystallisation. In the charge matched complexes the water, at least in some cases, appears to be involved mainly in aggregation and crystal formation,²⁰ whereas in the non-matched complexes it may play a more intimate role in the docking of the host and guest. Spectator ions, as in the complex of 5 and ferricyanide, may also be involved in the recognition phase of the process and they may also exert an influence on host-guest binding if they are not, as is commonly assumed, completely dissociated from the guest.

Experimental

Melting points were determined on a Reichert melting point apparatus and are uncorrected. Optical rotations were measured on an Optical Activity Ltd Polar 2000 automatic polarimeter. Mass spectra were recorded on a VG-ZAB mass spectrometer with Finnigan Incos II data system. ¹H NMR spectra were recorded at 400 and 300 MHz and ¹³C NMR spectra were recorded at 100 and 75 MHz on a Varian VXR-400 and a Bruker AC300 instrument, respectively.

Elemental analyses were carried out by the microanalytical section of the Chemistry Department, University College London. The polycation bromide salts, which are deliquescent, were extensively dried in vacuo but water of crystallisation remained.

Chemical reagents were purchased from Aldrich Chemical Co., Lancaster Synthesis, ACROS and BDH. Solvents and reagents were used as received except for tetrahydrofuran which was distilled over sodium and benzophenone under an atmosphere of nitrogen immediately prior to use. Analytical thin layer chromatography (TLC) was performed on pre-coated aluminium backed plates (Merck Kieselgel 60 F_{254}) and visualised using ultraviolet light (254 nm), iodine or potassium permanganate solution as appropriate.

4,6-Bis(bromomethyl)-1,2,3-trimethylbenzene. A solution of HBr in acetic acid (49% w/v, 11.5 mL) was added in one portion to a solution of paraformaldehyde (3.00 g, 100.0 mmol) and hemellitol (5 mL, 4.47 g, 40.0 mmol) in glacial acetic acid (250 mL). The resulting mixture was stirred at 100–110°C for 6 h and was then poured into water. A brown precipitate formed which was removed by filtration and washed exhaustively with water. The solid was then dissolved in acetone and re-precipitated by the addition of water. The mixture was then stirred for 2 h, and the solid was removed by filtration and dried under vacuum to give 4,6-bis(bromomethyl)-1,2,3-trimethylbenzene as a white solid (4.38 g, 14.3 mmol, 36%); mp 147–149°C, lit.³⁴ 153–154°C.

N-(11-Thioundecacyl)-DABCO bromide. 11-Bromo-1undecanethiol³⁵ (3.87 g, 14.5 mmol) was added to a solution of DABCO (2.91 g, 25.9 mmol) in acetonitrile (50 mL). The resulting mixture was stirred for 72 h and then poured into diethyl ether (600 mL) and stirred for 30 min. The white precipitate was removed by filtration, washed with diethyl ether, and dried under vacuum to give N-(11-thioundecacyl)-DABCO bromide as a white solid (5.23 g, 13.8 mmol, 95%); mp 260–262°C dec.; ¹H NMR δ (D₂O) 3.31 (t, 6H, J=7.4 Hz), 3.16 (m, 2H), 3.10 (t, 6H, J=7.5 Hz), 2.45 (t, 2H, J=7.1 Hz), 1.70–1.62 (br.m, 2H), 1.51 (m, 2H, J=7.3 Hz), 1.26, 1.21 (2 br.s, 15H); ¹³C NMR δ 97.7, 65.4, 52.9, 45.0, 34.0, 29.5, 29.4, 29.3, 29.1, 28.4, 26.5, 24.7, 22.0; IR 2918, 2850, 2450, 2346, 1466, 1317, 1099, 1057 cm⁻¹; MS *m/e* 299 (100, M–Br⁺), 266 (5); C₁₇H₃₅BrN₂S.H₂O requires C, 53.81; H, 9.83; N, 7.38; Br, 21.06. Found: C, 52.45; H, 9.24; N, 7.11; Br, 20.95.

3,6-Bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide (1). A solution of 3,6-bis(bromomethyl)-1,2,4,5tetramethylbenzene²⁷ (1.45 g, 4.5 mmol) in acetonitrile (50 mL) was added to a solution of DABCO (1.55 g, 13.8 mmol) in acetonitrile (100 mL) and the mixture was then stirred for 48 h. It was then poured into diethyl ether (300 mL) and the resulting mixture stirred for 30 min. A precipitate formed which was removed by filtration, washed with diethyl ether and dried under vacuum to give 1 a white solid (2.12 g, 3.9 mmol, 86%); mp 256–259 dec.; ¹H NMR δ (D₂O) 4.93 (s, 4H), 3.48 (t, 12H, *J*=7.3 Hz), 3.16 (t, 12H, *J*=7.8 Hz), 2.42 (s, 12H); ¹³C NMR (D₂O) δ 140.8, 128.6, 65.1, 54.4, 47.1, 21.4; IR 3010, 2961, 2889, 1653, 1497 cm⁻¹; MS *m/e* 463 (100, M–Br⁺), 383 (7, M–2Br⁺), 271 (33), 160 (29), 112 (71); C₂₄H₄₀Br₂N₄ requires C, 52.95; H, 7.35; N, 10.29. Found: C, 52.76; H, 7.14; N, 10.18.

2,5-Bis(DABCO-N-methyl)-1,4-dimethylbenzene dibromide (2). 2,5-Bis(bromomethyl)-1,4-dimethylbenzene²⁷ (1.00 g, 3.4 mmol) was added to a solution of DABCO (0.88 g, 7.8 mmol) in acetonitrile (100 mL) and the resulting mixture was stirred for 48 h. The mixture was then poured into Et₂O (300 mL) and stirred for 30 min. A precipitate was formed which was removed by filtration, washed with Et_2O , and dried under vacuum to give 2 as a white solid (0.96 g, 1.8 mmol, 53%); 238–240°C dec.; ¹H NMR δ (D₂O) 7.48 (s, 2H), 4.59 (s, 4H), 3.53 (t, 12H, J=7.4 Hz), 3.20 (t, 12H, J=7.2 Hz), 2.46 (s, 6H); ¹³C NMR (D₂O) 140.9, 140.2, 130.3, 67.9, 55.0, 47.2, 21.7; IR 2957, 2892, 1646, 1611 cm⁻¹; MS *m/e* 435 (100, M-Br⁺), 355 (7, M-2Br⁺), 243 (26), 132 (20); C₂₂H₃₆Br₂N₄, H₂O requires C, 49.45; H, 7.17; N, 10.48. Found: C, 50.03; H, 7.12; N, 10.63.

4,6-Bis(DABCO-N-methyl)-1,2,3-trimethylbenzene dibromide (3). 4,6-Bis(bromomethyl)-1,2,3-trimethylbenzene (1.34 g, 4.4 mmol) was added to a solution of DABCO (1.23 g, 11.0 mmol) in acetonitrile (180 mL), and the resulting mixture was stirred for 48 h. The mixture was then poured into Et₂O (400 mL) and stirred for 30 min. The resulting precipitate was removed by filtration and dried under vacuum to give 3 as a white solid (1.61 g, 2.8 mmol, 64%); mp 245–247°C dec.; ¹H NMR δ (D₂O) 7.36 (s, 1H), 4.66 (s, 4H), 3.45 (t, 12H, J=6.7 Hz), 3.16 (t, 12H, J=6.7 Hz), 2.41 (s, 6H), 2.32 (s, 3H); ¹³C NMR (D₂O) 144.3, 143.1, 140.1, 125.5, 68.9, 54.8, 47.2, 20.3, 19.3; IR 2987, 2961, 2947, 2886, 1459, 1363 cm⁻¹; MS m/e 449 (100, M-Br⁺), 369 (16, M-2Br⁺), 258 (61), 146 (56), 112 (49); C₂₃H₃₈Br₂N₄·2H₂O requires C, 48.77; H, 7.47; N, 9.89. Found: C, 49.16; H, 7.18; N, 10.02.

3,6-Bis(*N'*-**isopropyl-DABCO-***N*-**methyl**)-**1,2,4,5-tetramethylbenzene tetrabromide** (**4**). Isopropyl-DABCO bromide²⁶ (4.00 g, 17.0 mmol) was added to a solution of 3,6-bis(bromomethyl)-1,2,4,5-tetramethylbenzene²⁷ (2.00 g, 6.2 mmol) in acetonitrile (200 mL). The mixture was stirred for 72 h and the resulting solid was removed by filtration, washed with acetonitrile and dried under vacuum to give **4** as a white solid (4.15 g, 5.0 mmol, 81%); mp 249–251°C dec.; ¹H NMR δ (D₂O) 5.25 (s, 4H), 4.06 (br. t, 12H), 3.93– 3.87 (br. t, 14H), 2.46 (s, 12H), 1.46 (d, 12H, *J*=6.5 Hz); ¹³C NMR (D₂O) 141.6, 128.5, 71.3, 65.8, 53.7, 51.4, 21.6, 18.2; IR 2995, 2074, 1636, 1496, 1475 cm⁻¹; MS *m/e* 711 (8, M–Br⁺), 155 (100), 112 (3); C₃₀H₅₄Br₄N₄.2H₂O requires C, 43.60; H, 7.07; N, 6.78. Found: C, 43.96; H, 7.11; N, 6.84. 2,5-Bis(N'-isopropyl-DABCO-N-methyl)-1,4-dimethyl**benzene tetrabromide** (5). Isopropyl-DABCO bromide²⁶ (2.00 g, 8.5 mmol) was added to a solution 2,5-bis(bromomethyl)-1,4-dimethylbenzene²⁷ (1.00 g, 3.4 mmol) in acetonitrile (150 mL) and the mixture was stirred for 48 h. A solid formed which was removed by filtration, washed with acetonitrile and dried under vacuum to give 5 as a white solid (2.51 g, 3.1 mmol, 91%); mp 232-235°C dec.; ¹H NMR δ (D₂O) 7.58 (s, 2H), 4.93 (s, 4H), 4.14 (br. t, 12H), 3.98 (br. t, 14H), 2.52 (s, 12H), 1.49 (d, 12H, J=6.5 Hz); ¹³C NMR (D₂O) 141.5, 140.3, 130.0, 71.4, 68.2, 53.9, 51.4, 21.6, 18.2; IR 3022, 2053, 1625, 1488, 1473, 1122, 839 cm⁻¹; MS *m/e* 683 (26, M-Br⁺), 603 (4, $M-2Br^+$), 155 (100), 112 (4); $C_{28}H_{50}Br_4N_4 \cdot 3H_2O$ requires C, 41.19; H, 6.91; N, 6.86. Found: C, 41.09; H, 7.16; N, 6.69.

4,6-Bis(N'-isopropyl-DABCO-N-methyl)-1,2,3-trimethyl**benzene tetrabromide (6).** Isopropyl-DABCO bromide²⁶ (1.56 g, 6.6 mmol) was added to a solution 4,6-bis(bromomethyl)-1,2,3-trimethylbenzene³⁴ (0.50 g, 1.6 mmol) in acetonitrile (150 mL) and the mixture was stirred for 48 h. A solid formed which was removed by filtration, washed with acetonitrile and dried under vacuum to give 6 as a white solid (1.22 g, 1.5 mmol, 94%); mp 240-242°C dec.; ¹H NMR δ (D₂O) 7.52 (s, 1H), 5.00 (s, 4H), 4.06 (br. t, 12H), 3.94 (br. t, 14H), 2.47 (s, 6H), 2.36 (s, 3H, 1.47 (d, 12H, J=6.2 Hz); ¹³C NMR (D₂O) 145.4, 144.2, 139.4, 125.0, 71.3, 69.1, 53.8, 51.4, 20.3, 19.5, 18.2; IR 2991, 2903, 2050, 1635, 1476, 1443 cm⁻¹; MS *m/e* 697 (13, $M-Br^+$), 616 (3, $M-2Br^+$), 155 (100), 112 (3); C₂₉H₅₂Br₄N₄·3H₂O requires C, 41.95; H, 7.04: N, 6.75. Found: C, 42.23; H, 6.95; N, 6.62.

3.6-Bis(1-undecanethiol-N'-11-DABCO-N-methyl)-1,2,4,5tetramethylbenzene tetrabromide (7). 3,6-Bis(bromomethyl)-1,2,4,5-tetramethylbenzene²⁷ (0.25 g, 0.8 mmol) was added to a solution of N-(11-thioundecacyl)-DABCO bromide (0.72 g, 1.9 mmol) in acetonitrile (100 mL) and the resulting mixture was stirred for 48 h. A solid formed which was removed by filtration, washed with acetonitrile, and dried under vacuum to give 7 as a white solid (0.50 g,0.5 mmol, 57%); mp 265–269°C dec.; ¹H NMR δ (D₆-DMSO) 5.19 (s, 4H), 3.92 (br. m, 28H), 3.49 (br. m, 4H), 2.41 (s, 12H), 1.62 (br. m, 4H), 1.51 (br. m, 4H), 1.24 (br. s, 30H); ¹³C NMR (D₆-DMSO) 138.2, 126.1, 50.5, 49.8, 33.3, 28.9, 28.8, 28.7, 28.5, 28.3, 27.7, 25.5, 23.7, 21.3, 19.0; IR 2923, 2852, 2473, 2369, 1466, 1390, 1105, 1059 cm^{-1} ; MS *m/e* 998 (<1, M-Br⁺), 917 (<1, $M-2Br^+$), 299 (100), 112 (17); $C_{46}H_{86}Br_4N_4S_2\cdot H_2O$ requires C, 50.37; H, 8.09; N, 5.11. Found: C, 50.46; H, 8.16; N, 4.93.

2,5-Bis(1-undecanethiol-N'**-11-DABCO-**N**-methyl)-1,4-dimethylbenzene tetrabromide (8).** 2,5-Bis(bromomethyl)-1,4-dimethylbenzene ²⁷ (0.20 g, 0.7 mmol) was added to a solution of N-(11-thioundecacyl)-DABCO bromide (0.77 g, 2.0 mmol) in acetonitrile (100 mL) and the resulting mixture was stirred for 48 h. A solid formed which was removed by filtration, washed with acetonitrile, and dried under vacuum to give 8 as a white solid (0.38 g, 0.3 mmol, 50%); mp 243–247°C dec.; ¹H NMR δ (D₆-DMSO) 7.53 (s, 2H), 4.96 (s, 4H), 4.07, 3.91 (2 br. s, 28H), 3.51 (br. m, 4H), 2.44 (s, 6H), 1.63 (br. m, 4H), 1.51 (br. m, 4H), 1.25 (br. s, 30H); ¹³C NMR (D₆-DMSO) 137.7, 127.7, 63.4, 50.5, 50.0, 33.3, 28.9, 28.8, 28.7, 28.5, 28.4, 27.7, 25.5, 23.7, 19.3; IR 2994, 2924, 2852, 2372, 1466, 1389, 1107 cm⁻¹; MS *m/e* 972 (4, M–Br⁺), 677 (6), 591 (10), 299 (85), 154 (100), 112 (57); C₄₄H₈₂Br₄N₄S₂.2H₂O requires C, 48.62; H, 7.97; N, 5.15. Found: C, 48.39; H, 8.06; N, 5.15.

Polyanions

These were either obtained commercially or were prepared from the commercially available acids by treatment with the appropriate metal hydroxide followed by precipitation with acetone, isolation and drying under vacuum.

Crystallisation with ferro- and ferricyanide

A half saturated solution of the potassium ferro- or ferricyanide was added to a dilute solution of the polycation (concentration ca. 10 mg mL^{-1}) and, after standing, the precipitate was removed by filtration.

For the competitive experiment, a solution was made from equal volumes of saturated potassium ferricyanide and saturated ferrocyanide which was then added to a dilute solution of the polycation (concentration ca. 10 mg mL⁻¹). After standing the precipitate was removed by filtration.

NMR titrations and job plots

These were carried out as previously described.¹⁹

X-Ray structure analyses

Crystal data for **5**: $C_{74}H_{128}Fe_3KN_{26}O_{14} M$ 1812.67 g mol⁻¹, triclinic, $P\overline{1}$, a=16.2507(6), b=17.5519(6), c=18.0737(6) Å, $\alpha=79.734(1)$, $\beta=63.885(1)$, $\gamma=74.677(1)^\circ$, U=4452.9(3) Å, Z=3, data 14694, parameters 1180, R_1 [F²>2 σ (F²)] 0.0642, wR_2 (all data) 0.1187.

Crystals were mounted on a thin glass fibre using a fast setting epoxy resin and cooled on the diffractometer to 100 K using an Oxford Cryostream low temperature attachment. A total of 90 oscillation frames each of width 20 in ϕ and of 30 s exposure time were recorded using a Nonius KappaCCD diffractometer, with a detector to crystal distance of 25 mm. Crystals were indexed from the first ten frames using the DENZO package³⁶ and positional data were refined along with diffractometer constants to give the final unit cell parameters. Integration and scaling (DENZO, Scalepack³⁶) resulted in unique data sets corrected for Lorentz and polarisation effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction. Structures were solved using SHELXS-97³⁷ and developed via alternating least squares cycles and difference Fourier synthesis (SHELXL-97³⁷) with the aid of the program XSEED.³⁸ All calculations were carried out with either a Silicon Graphics Indy workstation or an IBM compatible PC. From systematically absent data and subsequent refinement the space group was found to be P-1. All non-hydrogen atoms were refined anisotropically.

Hydrogen atoms were generated in idealised positions, assigned an isotropic displacement parameter 1.2 times the atom to which they were attached (1.5 times for methyl groups) and a riding model adopted. Hydrogen atoms for disordered water molecules were not located. The K⁺ ion was found to be disordered over two sites, each of 50% occupancy. As a result extensive disorder was found for the hydrated portion of the structure. The 14 water molecules were modelled as occupying a total of 26 sites, with occupancies ranging from 1.0–0.25. A clear division in the difference Fourier map existed between the last partial water molecule and background. The CIF file of crystallographic data has been deposited with the Cambridge Crystallographic Data Service.

Acknowledgements

We thank Professor J. H. Ridd (UCL) for provision of the program for non-linear curve fitting to determine the K values, Dr A. J. Ibbett for valuable discussions, the EPSRC and King's College London for the provision of the X-ray diffractometer and the Nuffield Foundation for the provision of computing equipment. P. J. G. thanks the Leverhulme Trust for the award of an emeritus fellowship.

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