

Pentacoordinate Siliconate Tetraanionic Molecular Squares. Synthesis, Structure, and Solution Conformation of a Novel Tetraanion–Tetracation Ion Pair

Dianne J. McCord, James H. Small, John Greaves, Que N. Van, A. J. Shaka,*
E. B. Fleischer,* and K. J. Shea*

Contribution from the Department of Chemistry, University of California, Irvine California 92697-2025

Received April 9, 1998

Abstract: A tetraanionic molecular square containing four pentavalent siliconates is produced in high yield by the condensation of phenyltriethoxysilane and spirocatechol **1**. A single isomer, *meso* **2**, is produced from this diastereoselective condensation reaction. The steps leading up to the formation of *meso*-**2** are not known, but the reaction appears to be driven by the insolubility of the tetrakis(triethylammonium) salt **2a**. The tetraanionic macrocycle is a stable salt that undergoes ion-exchange reactions. An ion pair composed of the tetraanionic siliconate macrocycle and cyclobis(paraquat-*p*-phenylene) tetracation (**2e**) has been synthesized by ion exchange. Following complete assignment of all proton resonances in this 4×4 complex, the solution conformation was analyzed by an intermolecular double pulsed field gradient spin–echo (DPFGSE) NOE study. These results, aided by a molecular mechanics modeling study, have led to a proposed dynamic solution structure that features the cyclic bisparaquat tetracation selectively intercalating around a phenyl ring of the C_2 face of the macrocyclic tetraanion which in turn is engulfed by the *interior* of the tetraanion (Figure 10). This novel host–host complexation calls attention to the conformational flexibility of the macrocyclic tetrasiliconates and, in all probability, all macrocycles be they charged or neutral.

Introduction

Macrocycles play an integral part in the fields of supramolecular chemistry, nanotechnology, molecular recognition, self-assembly, and inclusion phenomena. Numerous organic macrocycles including cyclophanes, cyclodextrins, crown ethers, carcerands, cryptands, and cavitands have been developed and utilized in the above areas.^{1–11}

Macrocyclic polyions can expand the range of organizational forces for supramolecular assembly. Recently Stang,¹² Fujita,¹³ and Stoddart¹⁴ have described the synthesis of rigid *cationic* molecular squares and rectangles with $\sim 90^\circ$ bond angles as

building blocks for highly organized supramolecular structures.

We recently reported the first examples of *tetraanionic* molecular squares, macrocycles that contain four pentacoordinate siliconate groups that occupy the four faces of the square.¹⁵ In this paper we report details of the synthesis and characterization of these tetraanionic molecular squares and their ion-exchange chemistry. The resulting macrocyclic polyanion and polycation complexes mark the first steps in supermolecular architecture that utilize electrostatics as part of the organizational motif.

Pentavalent silicon possesses a conformational pliancy that complicates structural assignment. We have utilized ion-exchange chemistry to synthesize a novel bis macrocyclic tetraanion–tetracation ion pair. Insight into the remarkable solution structure and dynamic behavior of this ion pair was obtained by a combination of double pulsed field gradient spin–echo (DPFGSE) NOE experiments and computational analysis.

(1) *Supramolecular Chemistry*; Balzani, V., DeCola, L., Eds.; Kluwer Academic Publishers: The Netherlands, 1992.

(2) *Monographs in Supramolecular Chemistry 1 and 2*; Stoddart, J. F., Ed.; Royal Society of Chemistry: Cambridge, 1989, 1991.

(3) *Frontiers in Supramolecular Chemistry*; Schneider, H., Dürr, H., Eds.; VCH: Weinheim, 1991.

(4) *Inclusion Phenomena and Molecular Recognition*; Atwood, J. L., Ed.; Plenum: New York, 1990.

(5) *Molecular Inclusion and Molecular Recognition-Clathrates I*; Weber, E., Ed.; Topics in Current Chemistry 140; Springer-Verlag: New York, 1987. *Molecular Inclusion and Molecular Recognition-Clathrates II*; Weber, E., Ed.; Topics in Current Chemistry 149; Springer-Verlag: New York, 1987.

(6) Vögtle, F. *Cyclophane Chemistry*; J. Wiley & Sons: Chichester, 1993.

(7) Diederich, F. *Cyclophanes*; Royal Society of Chemistry: Cambridge, 1991.

(8) *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Vicens, J., Bohmer, V., Eds.; Kluwer Academic Publishers: The Netherlands, 1990.

(9) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: London, 1989.

(10) *Host–Guest Complex Chemistry: Synthesis, Structure, Applications*; Vögtle, F., Weber, E., Eds.; Springer-Verlag: Berlin, 1985.

(11) Iwamoto, T. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: New York, 1984; Vol. 1, p 29.

(12) (a) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502. (b) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273. (c) Stang, P. J.; Chen, K. *J. Am. Chem. Soc.* **1995**, *117*, 1667. (d) Stang, P. J.; Cao, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 4981. (e) Stang, P. J.; Zhdankin, V. *J. Am. Chem. Soc.* **1993**, *115*, 9808.

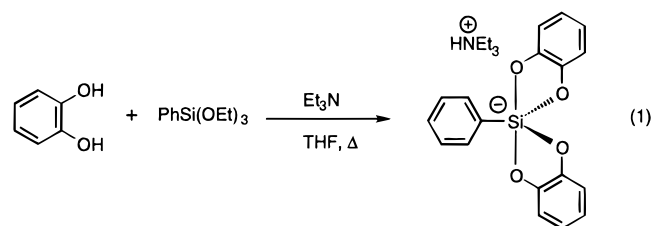
(13) (a) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (b) Fujita, M.; Nagao, S.; Iida, M.; Ogata, K.; Ogura, K. *J. Am. Chem. Soc.* **1993**, *115*, 1574. (c) Fujita, M.; Yazaki, J.; Ogura, K. *J. Am. Chem. Soc.* **1990**, *112*, 5645.

(14) (a) Brown, C. L.; Philip, D.; Stoddart, J. F. *Synlett*, **1991**, 462. (b) Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. *J. Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1547. (c) Ashton, P. R.; Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. *J. Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1550.

(15) (a) Small, J. H.; McCord, D. J.; Greaves, J.; Shea, K. J. *J. Am. Chem. Soc.* **1995**, *117*, 11588. For related macrocyclic anions: (b) Morgan, G.; McKee, V.; Nelson, J. *J. Chem. Soc., Chem. Commun.* **1995**, 1649. (c) Iwata, S.; Tanaka, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1491.

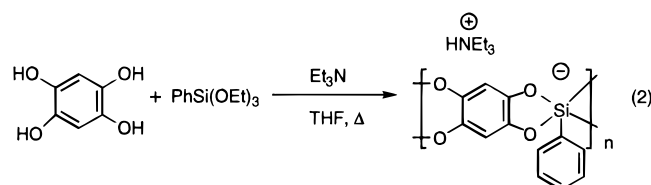
Results and Discussion

Penta- and hexacoordinate silicon species are involved as intermediates in substitution reactions at silicon.¹⁶ In the presence of multidentate and/or electronegative substitutes, stable, crystalline hypervalent siliconate derivatives can be prepared.¹⁷ One example, shown in eq 1, is the formation of



the crystalline hypervalent siliconate¹⁸ by condensation of catechol with phenyltriethoxysilane (PTES).

We have reported the synthesis of linear polymers and more highly condensed network materials that contain penta- and hexacoordinate silicon and germanium as an integral component of the polymer main chain.^{19–22} The polysiliconates were prepared by condensation of organotriethoxysilyl derivatives with biscatechols, such as 1,2,4,5-tetrahydroxy benzene. An

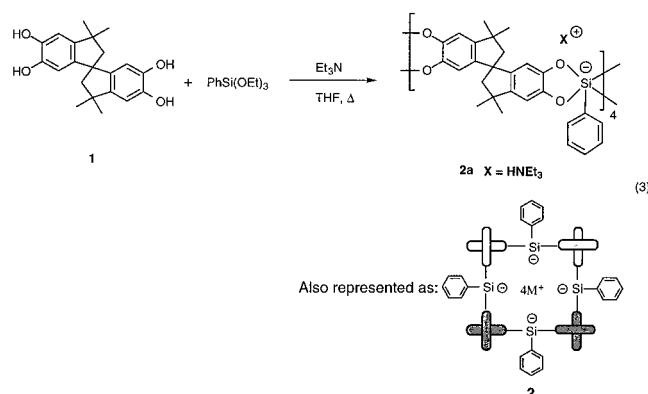


example of the synthesis of a ladder pentacoordinate siliconate ionomer is shown in eq 2.

Ongoing efforts to alter the ionomer properties including solubility and stability in organic solvents led to the exploration of these condensation polymerizations with structurally diverse biscatechols. One of the more interesting candidates was spirocatechol **1**, a C₂ symmetric angular biscatechol. The condensation reaction of **1** with PTES produced unexpected results.

When spirocatechol **1** was treated with an excess of PTES in refluxing THF containing 3 equiv of Et₃N, a white precipitate formed within 48 h in over 90% yield. A preliminary survey of the spectroscopic properties of the precipitate **2a** was puzzling. For example, the ¹H NMR (DMSO-*d*₆) revealed sharp resonances rather than the broad lines that are characteristic of oligomeric polysiliconates (i.e., eq 2). Also missing were characteristic resonances due to catechol “end groups.”^{20,22} The ¹³C NMR spectrum was also not that of an oligomeric mixture but more in line with a pure (albeit complex) substance. This observation, coupled with “normal” solution properties (low

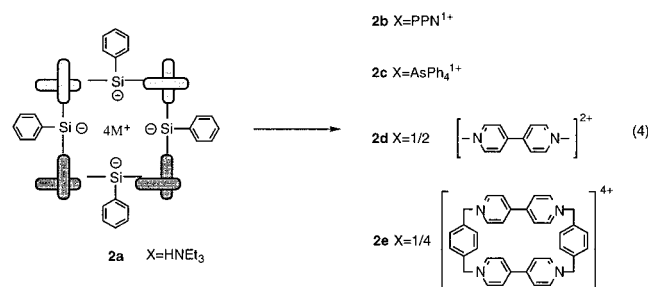
viscosity), suggested a low molecular weight cyclic structure. The first clues to the identity of **2a** came from liquid secondary ion mass spectrometry (LSIMS) in both positive and negative ion modes. The positive ion spectra showed two apparent odd-electron molecular ions that were consistent with [M + 4H]⁺ at 1768 Da and [M + Et₃NH + 3H]⁺ at 1870 Da (M = tetraanion core). The negative ion spectra gave a peak at 1767 Da corresponding to [M + 3H]⁻. The data are consistent with a tetrameric structure having a 441-Da repeat unit with appropriate counterions (eq 3). Vapor pressure osmometry also



provided a calculated molecular weight within 89% of the value expected for **2a**.

With a tentative assignment as the macrocyclic tetramer **2a**, we chose to explore the ion-exchange chemistry of the complex. Exchange of the weakly acidic triethylammonium ions with neutral cations was found to enhance the stability and solubility of the complex.

Cation exchange could be achieved in high yield (eq 4). For



example, treatment of **2a** with bis(triphenylphosphoranylidene)-ammonium chloride (PPNCl) in methylene chloride afforded, after extraction with water and recrystallization from methanol/water, a white solid (**2b**) in 96% yield. In a similar manner, **2c** could be obtained as a white solid in 94% yield by reacting **2a** with tetraphenylarsonium chloride in acetonitrile. Treatment of a saturated solution of **2a** in acetonitrile with a saturated solution of paraquat iodide in water resulted in the immediate formation of a reddish/purple precipitate **2d** in 70% yield. Likewise, treatment of a saturated solution of **2a** in acetonitrile with a saturated solution of cyclobis(paraquat-*p*-phenylene)-tetrakis(hexafluorophosphine),¹⁴ **3**, in acetonitrile yielded a purple precipitate **2e** in 71% yield.

LSIMS in the positive ion mode verified the ion-exchange products **2b–2e**. The spectra of the tetramer with the paraquat (PQT) cations, **2d**, exhibited the [M + 2PQT + H]⁺ signal at 2138.8 Da and a [M + PQT + 2H]⁺ signal at 1953.7 Da (Figure 1). Compounds **2c** and **2e** also exhibited the molecular ions associated with each of the calculated ion pairs but showed no

(16) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, 93, 1371.

(17) (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Stereochem.* **1986**, 131, 99. (b) Holmes, R. R. *Chem. Rev.* **1990**, 90, 17. (c) Corriu, R. J. P.; Young, J. C. in *The Chemistry of Organic Silicon Compounds*; S. Patai, Z. Rappoport, Eds.; Wiley: Chichester, U.K., 1989; Part 2, Chapter 20.

(18) Frye, C. L. *J. Am. Chem. Soc.* **1964**, 86, 3170.

(19) Shea, K. J.; Small, J. H.; Loy, D. A. *Chem. Mater.* **1992**, 4, 255. (20) Shea, K. J.; Loy, D. A.; Small, J. H. *Better Ceramics Through Chemistry V. MRS Symposium Proceedings*; 1992, Vol. 271, 711.

(21) Loy, D. A.; Small, J. H.; Shea, K. J. *Organometallics* **1993**, 12, 1484.

(22) Small, J. H.; Shea, K. J.; Loy, D. A.; Jamison, G. M. *ACS Symposium Series 585*; American Chemical Society: Washington, DC, 1995, 248.

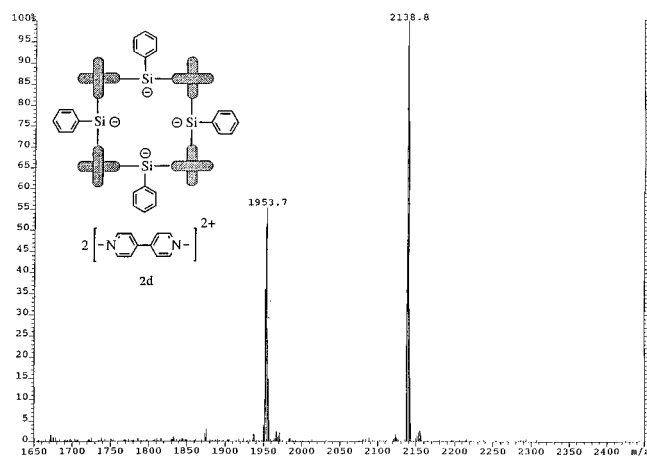


Figure 1. LSIMS of **2d**. The multiplet at m/e 2138.8 corresponds to the bis paraquat molecular ion (**2d**). The multiplet at m/e 1953.7 arises from exchange of two protons for one of the paraquat ions.

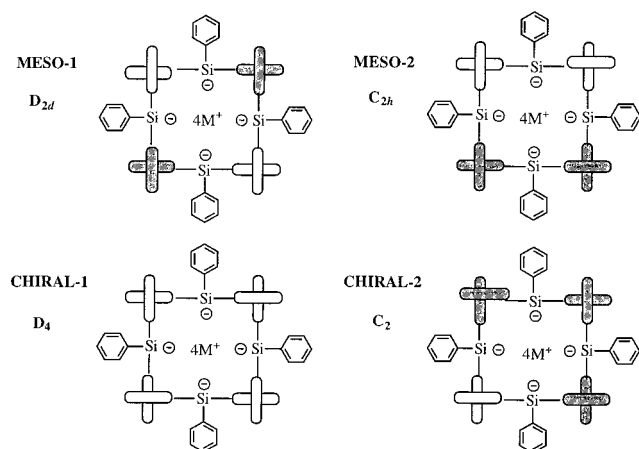


Figure 2. Schematic representation of the diastereomeric tetrasilicates. The *R* and *S* enantiomers of spirocatechol **1** are represented by differences in shading.

masses corresponding to the loss or exchange of counterions. Compound **2b** showed only the mass associated with one PPN counterion.

The preceding results establish that the macrocyclic siliconate tetramer is stable to ion-exchange chemistry. However, since the ^1H and ^{13}C NMR spectra of **2a–e** were consistent with discrete molecular species, the next task was to establish the structure of this species.

Microstructure Analysis by Multinuclear NMR Spectroscopy. There are six stereoisomeric cyclic tetramers that can be formed from racemic (C_2 symmetric) spirocatechol **1**, two *meso* diastereomers and two pairs of chiral isomers. A representation of their structures and a list of the point groups are given in Figure 2.²³ The siliconate core formed in near quantitative yield is a single stereoisomer. Analysis of *multinuclear* NMR spectra of **2a–d** permitted structural assignment of **2**.

Selected data used for this assignment included the observation of four discrete methyl resonances (excluding those from the $[\text{HNEt}_3]^+$ counterions) in both ^1H and ^{13}C NMR spectra of **2a**. The intensity ratio (1:1:1:1) of the methyl resonances

(23) Biscatecholates of phenyl triethoxysilane are trigonal bipyramidal. The constraints imposed upon the pentacoordinate silicon in the tetranuclear complex **2** may distort this geometry, however. The symmetry assignment of the squares is based upon a time-averaged symmetry at silicon. The barrier for pseudorotation is low (<12 kcal/mol) and appears to be not particularly sensitive to the geometry of the chelating ligand.¹⁷

Table 1. Chemical Shift Assignments for **2e**; The Designation Code is Found in Figure 8

proton designation	chemical shift (ppm)
BH ¹	7.70
BH ²	5.74
BH ³	8.86
BH ⁴	7.54
AH ¹	4.95
AH ²	5.48
AH ³	6.24
AH ⁴	6.72
AH ⁵	6.12
AH ⁶	5.82
AH ⁷	6.34
AH ⁸	7.35
AH ^{9,10}	7.04

remained invariant throughout recrystallization and ion exchange as well as during variable-temperature NMR studies ($25 \rightarrow 100$ °C). In addition, four methylene doublets were observed in the ^1H NMR spectra of **2a**. Solution ^{29}Si NMR spectra showed two resonances at -86.3 and -86.9 ppm. These values were characteristic of an aryl substituted pentacoordinate anionic siliconate.²² The ^{13}C NMR spectra of **2a** contained 25 resonances (excluding counterion contributions) which included eight sp^2 quaternary and eight sp^2 methine resonances. The nine resonances of the aliphatic region were composed of three quaternary and two methylene carbons in addition to the four methyl resonances.

The NMR spectral data is consistent with a *single* diastereomer, *meso-2*, formed in the condensation reaction (Table 1). The C_{2h} symmetry of this species predicts a total of 29 carbon²⁴ resonances (20 sp^2 and nine sp^3) associated with the tetraanion core. The remaining four carbon resonances were “resolved” in the ion-exchange product **2b**.

Formation of a single diastereomer, *meso-2*, is consistent with all of the NMR data. At present, the origin of this remarkable stereoselectivity is not known, but we have found that small changes in the formulation, for example, replacement of triethylamine with tributylamine or tolyl for phenyl in $\text{RSi}(\text{OEt})_3$, produces oligomeric mixtures rather than the cyclic tetramer.²⁵ It would appear that following formation of the cyclic tetramer the reaction is driven by the insolubility of the salt **2a** in THF. Once the cyclic tetramer has formed however, it can be recrystallized from a number of organic solvents without reversion to oligomeric materials.

Solution Conformation of 2e. The gross, time-averaged symmetry of the tetraanion core **2**, C_{2h} , can be extracted from analysis of its *multinuclear* NMR spectra. However, pentacoordinate silicon can undergo facile pseudorotation.¹⁷ Typical activation barriers for exchange of axial and equatorial positions fall close to 10 ± 3 kcal/mol.

The dynamic stereochemistry at silicon permits a number of conformations for the tetrasilicate core **2**. These structures range from a compact “figure eight” to conformations that include one or more Si–Ph groups directed *inside* the center of the core (Figure 3).

In addition, the -4 charge associated with the macrocyclic core presents a situation where the conformation of **2** can be strongly influenced by the dielectric of the medium *and* the nature and topology of the counterions.²⁶

(24) The symmetry unique proton, carbon, and silicon atoms in the four diastereomeric tetra spiro siliconates are *meso-1* (9:15:1); *chiral-1* (9:15:1); *meso-2* (18:29:2); *chiral-2* (30:51:2).

(25) McCord, D., unpublished results.

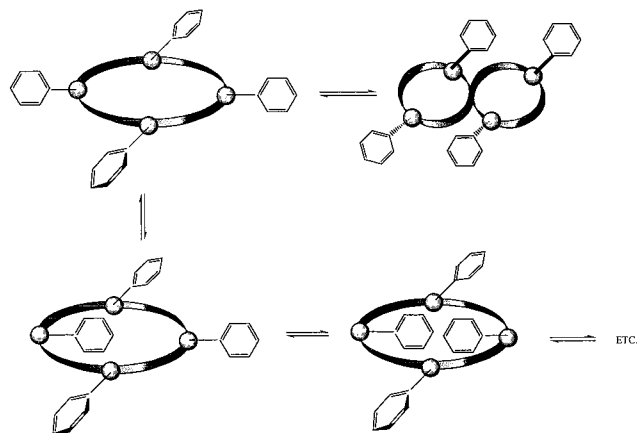


Figure 3. Schematic representation of the conformational possibilities of tetrasilicate **2**. The individual isomers can be generated by a combination of torsional rotations and Berry pseudorotations about the silicon–oxygen–carbon bonds.

Prompted by difficulties in the collection and analysis of suitable X-ray diffraction data,²⁷ we undertook an investigation of the solution conformation of **2** using NMR. We focused our attention on ion pair **2e**. This species has intriguing structural possibilities that include an intercalated ion pair. Particularly important for this analysis were *intermolecular* NOEs from DPGSE NOE experiments.²⁸ These experiments provided information regarding the time-averaged proximity of the two macrocyclic tetraions. The data generated from these experiments, coupled with computational studies, have provided a working model for what appears to be the rather remarkable dynamic solution behavior of this 4×4 complex.

An analysis of the solution structure of **2e** required the chemical shift assignments of all protons from both the cation and the anion. These data provided the basis for analysis of the NOE data.

Proton assignment was made from analysis of the spectra of the individual ions **2a**, **3**, and the ion pair **2e** (Figure 4) as well as that of the TOCSY spectra of **2e**.

These assignments are summarized in Table 1.

Although the aromatic resonances in both the anionic and cationic portions of the salt were somewhat broad in the ¹H NMR spectrum (DMSO-*d*₆, 500 MHz) at 20 °C, they remained invariant from room temperature to 100 °C. A comparison of the ¹H NMR spectra of **2a** and **2e**, as well as that of cyclobis(paraquat-*p*-phenylene)tetrakis(hexafluorophosphine), **3**, (Figure 4), provided evidence for selective (anisotropic) interactions between the cyclic tetraanion and the cyclic tetracation. Specifically, the ¹H NMR spectra of the tetraanion core contains *two* sets of aromatic resonances assigned to the two Ph–Si groups that reside on the *C*₂ and *σ* faces of the tetraanion core. Importantly, only one set of siliconate aromatic proton resonances was shifted upfield in **2e**, with the tetraanion proton AH¹ exhibiting the largest chemical shift of $\Delta\delta = -2.12$ ppm. This upfield shift suggests a strong association of the tetracation with *only one face of the tetraanion core*. The chemical shift

(26) Grunwald, E.; Highsmith, S.; I, T.-P. In *Ions and Ion Pairs in Organic Chemistry*; Szwarc, M., Ed.; John Wiley and Sons: New York, 1974; Vol. 2, pp 447–519.

(27) At present only thin needles of **2e** can be grown. Preliminary data collected on **2b** reveal a space group with monoclinic $Z > 1$. As a result of the complexity of the system and poor quality of the data set, it was not possible to solve the structure.

(28) (a) Hwang, T.-L.; Shaka, A. J. *J. Magn. Reson.* **1995**, *112*, 275. (b) Stott, K.; Stonehouse, J.; Keeler, J.; Hwang, T.-L.; Shaka, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 4199. (c) Emetaron, C.; Hwang, T.-L.; Mackin, G.; Shaka, A. J. *J. Magn. Reson.* **A1995**, *115*, 137.

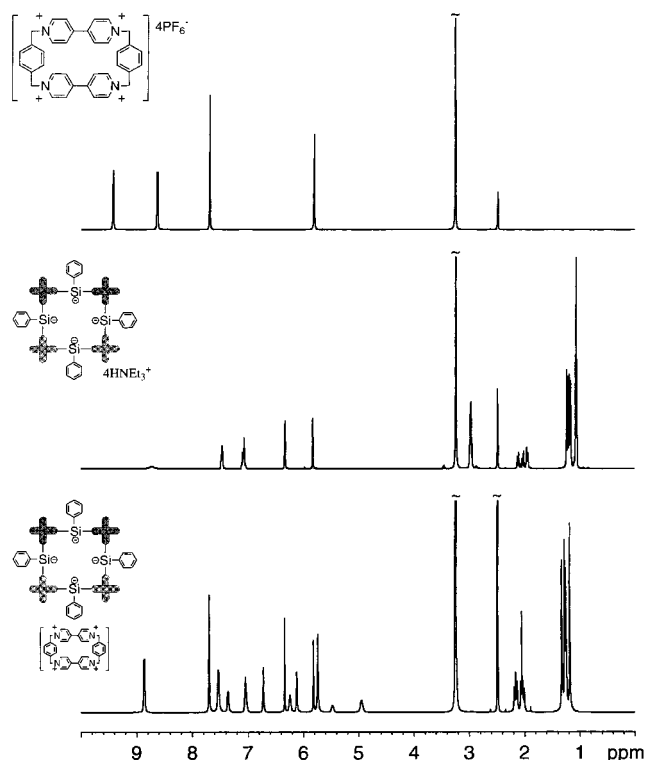


Figure 4. Stacked ¹H NMR plots of (a) cyclobis(paraquat-*p*-phenylene)tetrakis(hexafluorophosphine) **3**; (b) **2a**; and (c) **2e**.

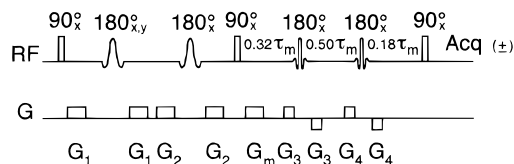


Figure 5. The transient 1D DPGSE NOE pulse sequence.^{28,29} The first two selective 180° pulses are optimized FM pulses derived from the well-known hyperbolic secant 180°-shaped pulse. Unwanted magnetizations recovering from *T*₁ relaxation during the mixing time were kept to a minimum by two broadband FM inversion 180° pulses.^{29,30} The two-step phase cycling is sufficient to accomplish the subtraction.

anisotropy is consistent with the siliconate phenyl occupying the *interior* of the cyclobis(paraquat-*p*-phenylene).¹⁴ A more detailed structural analysis of this 4×4 ion pair was obtained by an intermolecular NOE study.

Intermolecular NOE Interactions in 2e. A one-dimensional transient DPGSE NOE buildup study using 1.5, 3.0, and 6.1-mM samples of **2e** in DMSO-*d*₆ showed the rate of NOE buildups, whether they were intramolecular or intermolecular in origin, exhibited no concentration dependence. These observations led to a more detailed investigation of the structural relationship between the anion and cation.

The pulse sequence timing diagram for this NOE experiment is shown in Figure 5.

The excitation sculpting^{28,29} method, employing the double pulsed field gradient spin–echo (DPFGSE) sequence was used to excite a chosen resonance or group of resonances and simultaneously destroy all other magnetization. The target magnetization was then inverted with a 90° pulse at the start of the mixing time, τ_m . Broadband 180° pulses,³⁰ positioned as

(29) Stott, K.; Keeler, J.; Van, Q. N.; Shaka, A. J. *J. Magn. Reson.* **1997**, *125*, 302. (b) Van, Q. N.; Shaka, A. J. *J. Magn. Reson.* **1998**, *132*, 154.

(30) (a) Silver, M. S.; Joseph, R. I.; Hoult, D. I. *Phys. Rev. A* **1985**, *31*, 2753. (b) Baum, J.; Tycko, R.; Pines, A. *Phys. Rev. A* **1985**, *32*, 3435.

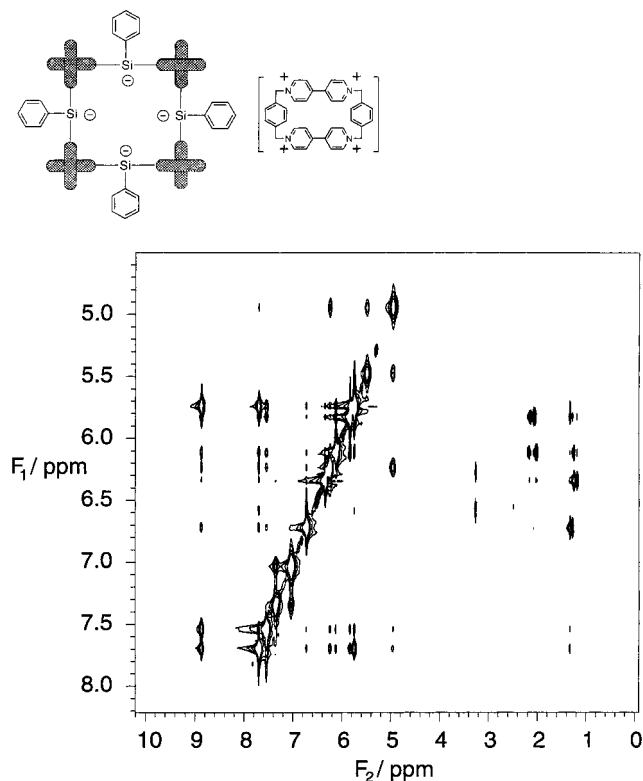


Figure 6. A transient 2D DPGFSE NOESY spectrum obtained from a 6.1 mM sample of **2e** at 500 MHz on a Varian *UnityPlus* spectrometer revealed interactions between the cyclic tetraanion, **2**, and the cyclic tetracation, **3**. A modified hyperbolic secant 180° -shaped pulse was used to selectively irradiate the region from 4.5 to 8.0 ppm for 3.673 ms. The mixing time was 300 ms.

shown (Figure 5), kept unwanted magnetization from T_1 relaxation quite small.²⁹ As described elsewhere,²⁹ these pulses do not appreciably affect the buildup of the NOEs. As a result, the DPGFSE NOE sequence will reliably detect tiny NOEs without problems from unwanted background signals that can arise from subtraction errors.

Selective irradiation of the 4.5–8.0 ppm region in a 2D DPGFSE NOESY experiment indicated the basic interactions occurring between (and within) the two ions (Figure 6). With foreknowledge that t_1 -noise from diagonal peaks may easily obscure the detection of minute intermolecular NOE cross-peaks, selective excitation using the DPGFSE method immediately eliminated all diagonal peaks outside the excitation bandwidth, revealing the weak desired cross-peaks.^{29b} The 1D transient DPGFSE NOE buildup from *each* key *target* signal was required to determine the exact interaction between the two cyclic units (parts a and b of Figure 7). As an extra precaution, the corresponding buildup experiments were carried out with the transmitter far removed from any resonances in the spectrum so that nothing was selectively irradiated by the double spin-echo. With the exception of three small solvent peaks, water, DMSO- d_6 , and acetonitrile, the baselines were absolutely clean and flat. Efficient suppression of artifacts in the regions of interest allowed NOEs as small as 0.3% to be detected with confidence, limited only by signal-to-noise.

Figure 8 shows the symmetry unique portions of the siliconate ionomer *meso-2* and summarizes the important interior interactions. The phenyl ring bearing protons AH^1 – AH^3 is on the C_2

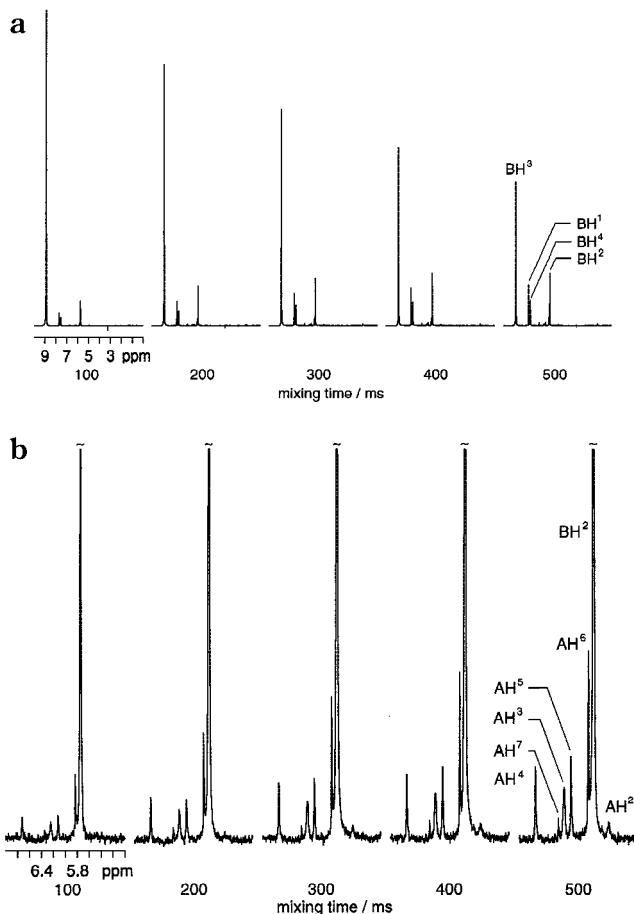


Figure 7. The 1D transient DPGFSE NOE buildup. (a) The proton BH^3 of the cyclic tetracation, **3**, from a 6.1 mM sample of **2e**, was irradiated for 35.650 ms using an FM selective 180° -shaped pulse. The full NOE buildup spectra are shown for five different mixing times. (b) The region from 5.0–7.0 ppm of a were plotted with the vertical scale enlarged by 20 times to show the small *intermolecular* NOE buildups of the protons AH^2 , AH^3 , AH^4 , AH^5 , and AH^6 on the C_2 face of the anion, and the proton AH^7 on the C_{2h} face of **A**.

face of the tetraanion **2**, and the phenyl ring containing protons AH^8 – AH^{10} is on the face with the mirror plane of the C_{2h} symmetric tetraanion **2**. On the C_2 face of the tetraanion, each of the protons AH^1 – AH^5 displayed NOE interactions with each of the protons BH^1 , BH^3 , and BH^4 of the cation **3**. It is well-documented by Stoddart et al. that the cyclobis(paraquat-*p*-phenylene) tetracation will adopt a π -stacked conformation with other aromatic rings.^{14,31} On the basis of this literature precedent as well as the differential response in chemical shift of the two Si phenyl rings upon formation of **2e** and information obtained from the 1D DPGFSE NOE buildups, an interaction of the type illustrated in Figure 8, in which the phenyl ring on the C_2 face of **2** is intercalated in the cyclobis(paraquat-*p*-phenylene) at least for a brief time, is supported.

These same strong interactions were *not* observed on the face with the mirror plane of **2**. There is, however, a very strong NOE interaction from AH^6 with all three aromatic protons BH^1 , BH^3 , and BH^4 of cyclobis(paraquat-*p*-phenylene). These interactions were confirmed by irradiation of BH^1 , BH^3 , and BH^4 and by observing the buildup on AH^6 . This is indicated by the double-ended arrows in Figure 8. Selective irradiation of the $AH^{9,10}$ protons gave the expected NOEs to AH^8 to the phenyl ring on the C_2 face and an extremely small NOE to only BH^1 of the cation **3**. It is possible that on this face the steric hindrance created by the gem dimethyls of the spirocatechol

(31) (a) Ballardini, R.; Balzani, V.; Credi, A. J.; Brown, C. L.; Gillard, R. E.; Montalti, M.; Philip, D.; Stoddart, J. F.; Venturi, M.; White, J. P.; Williams, B. J.; Williams D. J. *J. Am. Chem. Soc.* **1997**, *119*, 12503.

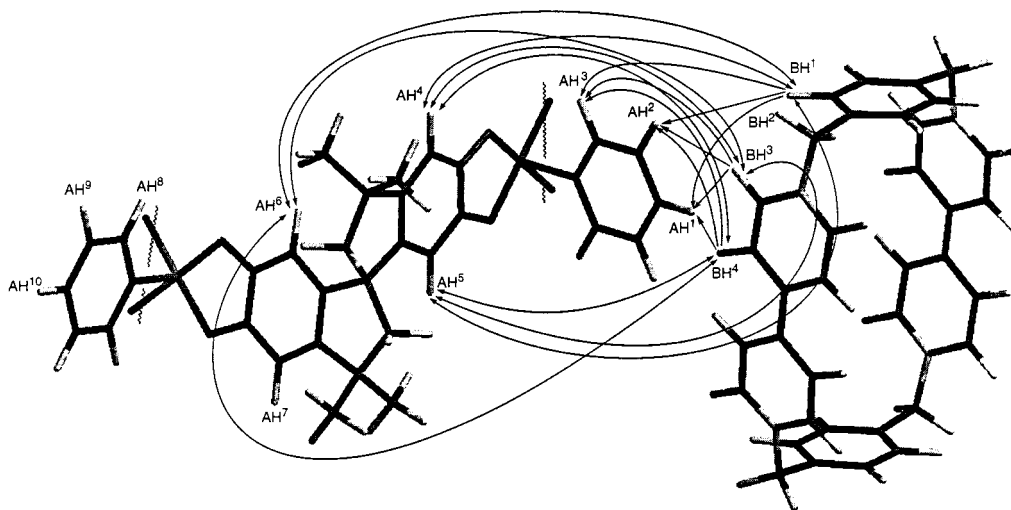


Figure 8. Summary of the intermolecular NOE interactions in **2e**. The macrocyclic tetra anionic siliconate **2** is represented in truncated form showing only symmetry unique protons on the C_2 and σ "faces" of the macrocycle.

does not permit the tetracation to approach closely the phenyl substituent as observed on the C_2 face (vide infra). The electrostatic force between the hypervalent silicon and the pyridinium unit, however, may be great enough to bring the two ions in **2e** within the extremely sensitive detection limits for these NOE experiments (<5 Å). The structure that emerges is one of a *selective* intercalation of the bisparaquat tetracation by the aromatic rings on the C_2 faces of the tetraanion core **2** but little interaction, if any, with the corresponding phenyls on the σ face. This finding is consistent with the selective upfield shift of only *one* set of Si-phenyl groups upon ion exchange with cyclic bisparaquat **3**. In addition to this anisotropic intercalation, there remained the *very* puzzling strong intermolecular NOEs of the bisparaquat tetracation and AH^6 . A simple intercalation of the ion pair depicted in Figure 8 does not account for this interaction. In an effort to explore possible structures that could account for the observed NOEs, a computational study of this ion pair was undertaken.

Molecular Modeling of 2e. Molecular mechanics studies were carried out with the BIOSYM package from Molecular Simulations. The programs employed were the Insight and Discover modules (Version 3.0.0) with the *ESFF* force field. The molecular mechanics were run until the systems refined to at least a derivative of less than 0.01 kcal. The dielectric constant can have a fairly large effect on these systems because of the high charge of the anion (-4) and cation ($+4$). For these studies, the dielectric constant was held at 4.0. The molecules were computed with no solvent.

Calculations were performed on the core tetrasiliconate anion **2a** in the absence of any counterions. The minimized structure is roughly rectangular. (The coloring scheme, Figure 9a, allows identification of the 2-fold and mirror faces of the molecule.) The Si-Si distance that lies on the 2-fold axis is 15.53 Å, while the Si-Si distance on the mirror plane is calculated to be 15.25 Å.

When the tetracation **3** is placed over either the C_2 phenyl or the σ phenyl and the structure is minimized, the macrocyclic polycation is found to fit best over the siliconate phenyl on the C_2 axis. Intercalation of the σ phenyl is less favored due to nonbonded interactions. These two modes of association of tetracation and tetraanion **2e** are shown in a composite representation in Figure 9b.

The finding that the tetracation should selectively host only *one* pair of siliconate phenyl rings is consistent with the NMR

analysis which shows shielding of only one set of Si-Ph resonances upon formation of **2e** (Figure 4). A structure that incorporates intercalation of the C_2 siliconate phenyls by the tetracation accounts for many but not all of the observed NOEs. In particular this structure does *not* account for some of the strongest NOEs that are observed between the tetracation and the tetraanion AH^6 protons (Figure 8).

In an effort to generate additional structures for consideration, calculations were initiated by placing the tetracation within 8–10 Å of the center of the tetraanion. This minimization resulted in siliconate phenyl-tetracation intercalation as before but with an additional feature that involved siliconate pseudorotation of the intercalated phenyl to the *interior* of the tetraanion cavity (Figure 10). The known propensity of silicon to undergo facile pseudorotation³² and the capacity of the tetraanion interior to readily accommodate the tetracation "host" provides for a structure that optimizes both electrostatic interactions and van der Waals contacts. Importantly this novel host-host structure satisfies all of the observed NOEs including the puzzling strong interactions between the siliconate tetraanion and protons AH^6 on the tetracation (Figure 8). The Si-Si distances in this structure are 8.61 Å along the 2-fold axis and 16.76 Å along the mirror plane. A time-structure-energy profile of the tetracation-tetraanion interaction reveals that substantial structural reorganization takes place upon ion pair formation. This large complexation-induced conformational change is likely to be a common occurrence when highly charged systems interact to form new molecular species.

The C_{2h} time-averaged symmetry of **2e** provides fascinating insight into the dynamics of the ion pair. The two siliconate phenyls on the C_2 face are equivalent. This requires that the ion pair in Figure 10 undergo a rapid *intramolecular* exchange (via a tight ion pair?) so that the tetracation can associate equally with both C_2 phenyls. This would require an unraveling of the host-within-a-host to permit exchange between the two structures.

The situation concerning *intermolecular* exchange between ion pairs is not as clear, but studies of stability constants and exchange rates of ion pairs, including closely related tetraanions and tetracations, permit estimates of this process. Intermolecular exchange will be limited by the off-rate or dissociation of the ion pair (k_{diss}). Schneider has determined the equilibrium

(32) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927.

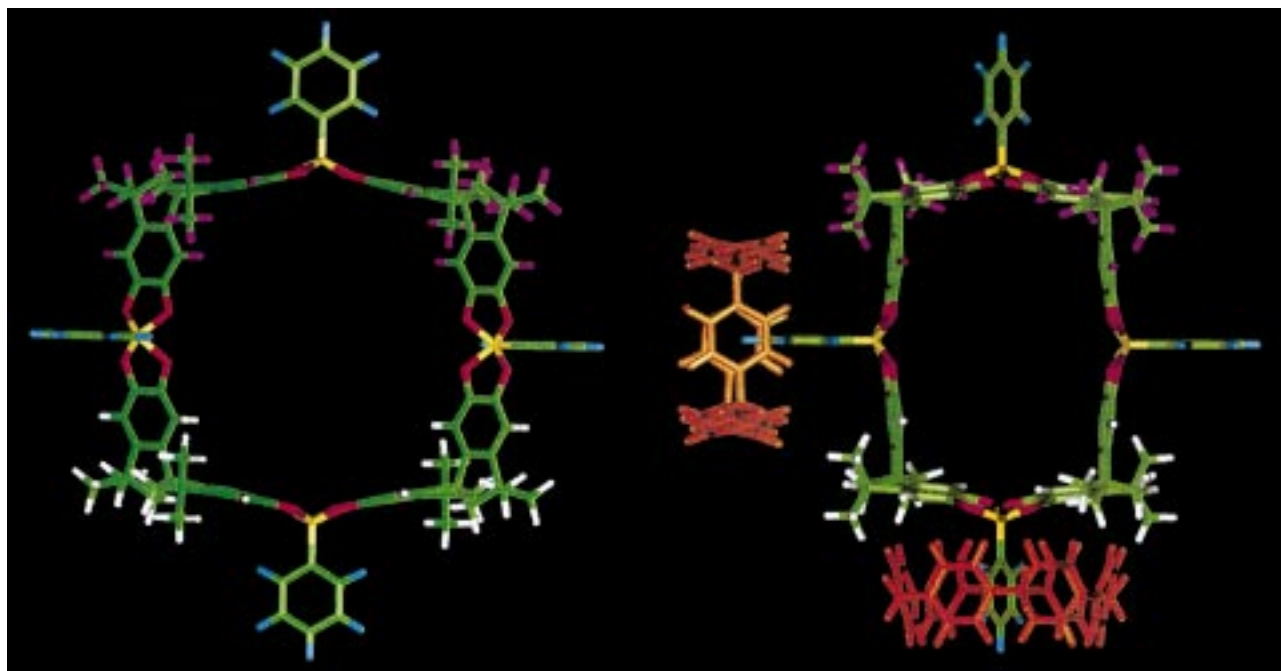


Figure 9. (Left) Computer-derived structures for the core tetrasiliconate *meso*-2. The coloring scheme used in these Figures is green for carbon on the tetraanion, red for the oxygens, yellow for the silicons, blue for the nitrogens, and orange for the carbons and hydrogens on the tetracation. The hydrogens on the siliconate are white for the *R* enantiomers of the spirocatechol and pink when on the *S* isomer. The light blue are the hydrogens that are attached to the silicon-complexed phenyl groups. (Right) Composite representation of two possible interaction modes between cyclobis(paraquat-*p*-phenylene) tetracation **3** and the core tetrasiliconate **2**. The siliconate phenyl on the C_2 face is found to intercalate more readily than that on the σ face.



Figure 10. Proposed structure for the 4×4 complex **2e**. The time-averaged symmetry of the complex requires a dynamic equilibrium between the tetra cation **3** and *both* siliconate phenyls on the C_2 faces of **2**.

constants of multiply charged ion pairs in water and alcohol solutions.³³ These studies provide estimates of coulomb and van der Waals contributions to the free energy of complexation (ΔG_{AB}) of ion pairs. The association constants of ion pairs composed of multiply charged cations and anions are dominated by electrostatics. From the derived empirical parameters one

can estimate ΔG_{AB} for **2e** to be approximately 20–25 kJ/mol. Schneider and others have also measured the association rates of selected ion pairs and found them, not surprisingly, to be diffusion-controlled.³⁴ Using the diffusion limit for the on rate and the calculated free energy of association one can estimate the off-rate. For our system and several closely related ion pairs studied by Schneider, these rates fall within a range of 10^5 to 10^3 s⁻¹. These exchange rates are fast at room temperature on the time scale of the NMR experiment. Thus both inter- and intramolecular exchange processes should proceed rapidly under the experimental conditions.

Summary

Molecular squares containing four pentavalent siliconates are produced in high yield by the condensation of phenyltriethoxy silane and spirocatechol **1**. The resulting tetraanionic macrocycle is a stable compound that readily undergoes ion-exchange reactions. A single diastereomer, *meso*-**2**, is produced from this condensation reaction. The sequence of reactions that leads to the formation of *meso*-**2** is not at this time known, but the reaction appears to be driven by the insolubility of salt **2a**. A tetraanion–tetracation ion pair **2e** has been synthesized by an ion-exchange reaction. Complete assignment of all protons in this 4×4 complex permitted an inter- and intramolecular NOE study in DMSO solutions of the ion pair. An analysis of these results, aided by a molecular mechanics modeling study, has led to the proposal of a 4×4 complex that features the bisparaquat tetracation selectively intercalating a phenyl ring on the C_2 face of the macrocyclic tetraanion which in turn is engulfed by the *interior* of the tetraanion (Figure 10). The exchange of the tetracation between the phenyl groups on the individual C_2 faces must be occurring rapidly (sub millisecond

(33) Schneider, H.-J.; Schiestel, T.; Zimmerman, P. *J. Am. Chem. Soc.* **1992**, *114*, 7698.

(34) (a) Schneider, H.-J.; Kramer, R.; Simora, S.; Schneider, U. *J. Am. Chem. Soc.* **1988**, *110*, 6442. (b) Schneider, H.-J.; Guttes, D.; Schneider, U. *J. Am. Chem. Soc.* **1988**, *110*, 6449.

time scale). These results call attention to the conformational mobility of macrocyclic rings and the potential influences of counterion topology on ion pair structure. The approach of the tetracation produces a substantial structural reorganization in the tetraanion. This novel host–host complex is a consequence of optimizing the Coulombic attractions and van der Waals contacts in the ion pair.

Experimental Section

General Methods. Routine proton, carbon-13, and silicon-29 NMR spectra were obtained using a General Electric GN-500 or a Bruker IBM AC 300 spectrometer and were recorded in DMSO-*d*₆ at room temperature unless otherwise specified. Chemical shifts, δ , are expressed in ppm downfield from tetramethylsilane, using the residual DMSO as an internal standard for ¹H and ¹³C NMR spectra. ²⁹Si NMR spectra were referenced to tetramethylsilane as an external standard. Coupling constants are expressed in hertz.

DPFGSE NMR spectra were recorded on a Varian *UnityPlus* 500 MHz spectrometer. Infrared spectra were recorded on an Analect RFX-40 FTIR as pressed pellets (KBr). CIMS were obtained on a VG7070e high-resolution mass spectrometer. LSIMS (mNBA matrix) were obtained using a VG-Autospec high-resolution mass spectrometer in the positive ion mode using a Cs ion gun.

Solvents and silanes were rigorously dried and distilled from appropriate drying agents unless otherwise noted, and all other chemicals were of reagent quality and were used as obtained from the manufacturers. Reactions were performed in an argon atmosphere when necessary. Gas chromatography (GC) experiments were run on a HP model 5890 FID gas chromatograph using a DB-5 capillary column.

Tetranuclear Macrocyclic Siliconate Ionomer, X = HNET₃ (2a). To a refluxing solution of 5,5',6,6'-tetrahydroxy-1,1'-spiro-bis(indane) (1.50 g, 4.40 mmol) and phenyltriethoxysilane (1.11 g, 4.44 mmol) in anhydrous THF (11 mL) was added dropwise rapidly dry triethylamine (1.34 g, 13.2 mmol). The mixture was stirred and heated under reflux in an argon atmosphere for 4 days with the formation of a white precipitate occurring within 48 h. After the mixture was cooled to room temperature, the precipitate was collected by filtration and rinsed with THF (100 mL). Residual solvent was removed from the precipitate in vacuo yielding 1.73 g (80%) of pure product. (Use of excess phenyltriethoxysilane resulted in a higher yield of product (95%).) ¹H NMR (500 MHz) δ 8.75 (br s, 4H), 7.47 (m, 8H), 7.09 (m, 12H), 6.36 (s, 4H), 6.34 (s, 4H), 5.84 (s, 4H), 5.82 (s, 4H), 2.95 (q, 24H, *J* = 7.28), 2.12 (d, 4H, *J* = 12.63), 2.03 (d, 4H, *J* = 12.66), 1.95 (d, 4H, *J* = 12.44), 1.94 (d, 4H, *J* = 12.76), 1.24 (s, 12H), 1.21 (s, 12H), 1.19 (s, 12H), 1.17 (s, 12H), 1.04 (t, 36H, *J* = 7.29); ¹³C NMR (125 MHz) δ 149.4, 149.3, 142.5, 142.3, 140.1, 139.4, 139.2, 138.1, 134.8, 134.6, 127.5, 127.4, 126.7, 104.5, 104.3, 102.5, 59.8, 59.6, 57.1, 45.7, 42.4, 42.3, 32.0, 31.6, 31.1, 30.7, 8.5; ²⁹Si NMR (99 MHz, DMSO-*d*₆) δ -86.3, -86.9; FTIR (KBr) ν 3442, 2951, 2861, 1637, 1485, 1361, 1279, 1224, 1116, 865, 833, 742, 705, 601 cm⁻¹. Elemental analysis calcd for C₁₃₂H₁₆₄N₄O₁₆Si₄: C, 72.89; H, 7.60; N, 2.58; Si, 5.16. Found: C, 72.68; H, 7.94; N, 2.13; Si, 5.24.

Tetranuclear Macrocyclic Siliconate Ionomer X = PPN (2b). A solution of bis(triphenylphosphoranylidene)ammonium chloride (PPNCl) (0.290 g, 0.512 mmol) in dry CH₂Cl₂ (12 mL) was added dropwise rapidly to a solution of **2a** (0.280 g, 0.128 mmol) in dry CH₂Cl₂ (12 mL). After the mixture was stirred at room temperature for 4 h, the organic layer was extracted with water (4 × 20 mL). The solvent was removed in vacuo, and the white solid was purified by precipitation from MeOH using H₂O. Yield: 0.48 g (96%); ¹H NMR (500 MHz) δ 7.70–7.32 (m, 128 H), 7.06 (s, 6H), 6.80–6.60 (m, 6H), 6.30 (s, 8H), 5.92 (s, 4H), 5.71 (s, 4H), 2.10–1.83 (m, 16H), 1.19 (s, 12H), 1.17 (s, 12H), 1.13 (s, 12H), 1.10 (s, 12H); ¹³C NMR (125 MHz) δ 149.6, 149.5, 149.3, 142.8, 142.4, 139.8, 139.2, 139.0, 137.8, 135.2, 135.1, 135.0, 133.6, 131.9, 129.4, 129.3, 127.4, 127.2, 127.1, 126.5, 126.3,

104.6, 104.5, 102.3, 102.2, 59.8, 59.7, 57.0, 42.3, 42.2, 31.9, 31.5, 31.1, 30.6; FTIR (KBr) ν 3062, 3022, 2951, 2927, 2858, 1630, 1494, 1446, 1369, 1285, 1234, 1192, 1125, 1006, 881, 842, 753, 730, 701 cm⁻¹.

Tetranuclear Macrocyclic Siliconate Ionomer, X = AsPh₄ (2c). A saturated solution of tetraphenylarsonium chloride hydrate (0.162 g, 0.372 mmol) in CH₃CN was added dropwise to a saturated solution of **2a** (0.200 g, 0.0922 mmol) in CH₃CN. The mixture was stirred for 16 h. After 16 h, H₂O was added to precipitate the desired product. The precipitate was washed with copious amounts of H₂O and dried in vacuo. Yield of white solid: 0.186 g (94%); ¹H NMR (500 MHz) δ 7.84–7.33 (m, 84H), 7.06 (s, 8H), 6.71–6.58 (m, 8H), 6.33 (s, 4H), 6.29 (s, 4H), 5.91 (s, 4H), 5.69 (s, 4H), 2.09 (d, 4H, *J* = 12.1), 2.03 (d, 4H, *J* = 12.1), 1.94 (d, 4H, *J* = 12.4), 1.88 (d, 4H, *J* = 12.2), 1.20 (s, 12H), 1.18 (s, 12H), 1.15 (s, 24H); ¹³C NMR (125 MHz) δ 149.5, 149.4, 142.6, 142.1, 139.9, 139.4, 139.1, 138.2, 135.4, 135.1, 134.3, 133.1, 130.9, 129.5, 127.5, 126.6, 126.3, 120.9, 104.5, 102.4, 102.3, 59.7, 59.6, 57.0, 42.4, 31.9, 31.6, 31.1, 30.7; IR (KBr) ν 3065, 3024, 2956, 2931, 2863, 1643, 1493, 1448, 1367, 1287, 1233, 1117, 1088, 1005, 879, 841, 748, 700 cm⁻¹; high-resolution LSIMS calcd for C₂₀₄H₁₈₀As₄Si₄O₁₆ M⁺ 3296.9, found 3296.9.

Tetranuclear Macrocyclic Siliconate Ionomer X = 1/2[PQT] (2d). A saturated solution of paraquat iodide (0.0820 g, 0.186 mmol) in H₂O was added dropwise to a saturated solution of **2a** (0.200 g, 0.0922 mmol) in CH₃CN. A red/purple precipitate formed immediately. The mixture was stirred 12 h, and the precipitate was collected by filtration. After the precipitate was rinsed with excess H₂O/CH₃CN (1:2), the solid was dried in vacuo. Yield: 0.139 g (70%); ¹H NMR (500 MHz) δ 8.93 (d, 4H, *J* = 6.1 Hz), 8.38 (d, 4H, *J* = 6.1 Hz), 7.50–7.48 (m, 4H), 7.43 (d, 4H, *J* = 7.1 Hz), 7.09 (t, 8H, *J* = 2.9 Hz), 7.06 (t, 2H, *J* = 7.4 Hz), 6.90 (t, 2H, *J* = 7.2 Hz), 6.38 (s, 4H), 6.36 (s, 4H), 5.82 (s, 4H), 5.79 (s, 4H), 4.26 (s, 12H), 2.12 (d, 4H, *J* = 12.5 Hz), 2.04 (d, 4H, *J* = 12.5 Hz), 1.93 (2 overlapping d, 8H, *J* = 11.6 Hz), 1.23 (s, 12H), 1.21 (s, 12H), 1.19 (s, 12H), 1.16 (s, 12H); ¹³C NMR (125 MHz) δ 149.2, 149.1, 147.8, 146.4, 142.5, 142.0, 140.2, 139.8, 139.3, 138.2, 134.8, 134.3, 127.6, 127.5, 127.0, 126.7, 125.7, 104.3, 102.7, 59.6, 59.4, 57.1, 47.9, 42.4, 42.3, 31.9, 31.5, 30.9, 30.7; ²⁹Si NMR (99 MHz) δ -86.4, -86.8; IR (KBr) ν 3130, 3066, 2964, 2974, 1654, 1577, 1500, 1371, 1294, 1243, 1127, 896, 858, 755, 717 cm⁻¹.

Tetranuclear Macrocyclic Siliconate Ionomer 1/4Cyclobis(paraquat-*p*-phenylene) (2e). A saturated solution of cyclobis(paraquat-*p*-phenylene)tetrakis(hexafluorophosphine)¹⁴ (0.0103 g, 0.00922 mmol) in CH₃CN was added to a saturated solution of **2a** (0.0200 g, 0.00934 mmol) in CH₃CN. Purple precipitate formed immediately. After the mixture was stirred for 2 h, the precipitate was collected by filtration, washed with CH₃CN, and dried in vacuo to yield 0.0150 g (71%) of product which turned grayish upon drying. ¹H NMR (500 MHz) δ 8.86 (s, 8H), 7.70 (s, 8H), 7.54 (s, 8H), 7.35 (br s, 4H), 7.04 (2 overlapping signals, 6H), 6.72 (s, 4H), 6.34 (s, 4H), 6.24 (br s, 4H), 6.12 (s, 4H), 5.82 (s, 4H), 5.74 (s, 8H), 5.48 (br s, 2H), 4.95 (br s, 4H), 2.19–2.01 (m, 16H), 1.32 (s, 12H), 1.27 (s, 12H), 1.25 (s, 12H), 1.18 (s, 12H); ¹³C NMR (125 MHz) δ 149.5, 149.2, 149.0, 146.3, 144.3, 140.3, 140.0, 139.8, 138.3, 136.8, 134.6, 133.5, 130.1, 126.6, 125.9, 125.4, 125.3, 104.5, 104.0, 103.9, 103.0, 102.8, 63.8, 59.5, 59.2, 57.1, 42.6, 42.5, 32.0, 31.8, 30.8; IR (KBr) ν 3126, 3059, 2959, 2866, 1640, 1493, 1367, 1287, 1233, 1165, 879, 844, 790, 748, 712 cm⁻¹; high-resolution LSIMS calcd for C₁₄₄H₁₃₂N₄Si₄O₁₆ M⁺ 2284.9, found 2284.7.

Acknowledgment. K.J.S. acknowledges support from the NSF. Q.N.V. acknowledges support from a Synthesis and Structure of Biological Macromolecules Training Grant (T32 GM 07311-23). This work was also supported by an NSF Grant (CHE-9625674) and the Dreyfus Foundation Teacher-Scholar Award.

JA981201U