

# Self-assembled macrocycles with pentavalent silicon linkages

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## Abstract

Organic substrates containing two catechol (*ortho*-dihydroxybenzene) components at opposite ends self-assemble with a silicon substrate containing three nucleofugic groups (methoxy or ethoxy) under basic conditions to produce macrocycles ranging from monomers to pentamers. Silicon in all the macrocycles is pentacoordinate, negatively charged, and possessed of one organic monodentate ligand attached via carbon and two catechol bidentate ligands attached via oxygen. The organic materials with the two catechol structures thus serve as struts between the corners provided by the pentacoordinate silicon atoms.

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**Keywords:** Macrocycles; Pentacoordinate silicon; Self-assembly

## 1. Introduction

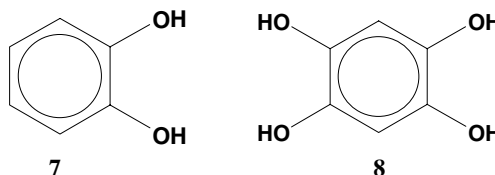
The reaction of transition metals with organic linkages has led to a rich assortment of molecular geometries, including the equivalents of squares, pentagons, hexagons, cubes, tetrahedra, and double hexagons [1–9]. These molecules have been designed to have high structural integrity, adjustable cavities, high surface area, and uniform pores to serve as new materials for ion exchange, sensor applications, molecular or chiral recognition, catalysis, environmental remediation, and drug delivery.

To date, very little work has occurred in which main group elements, silicon in particular, have been used to serve in lieu of transition metals as the link between the organic entities. Silicon-based, self-assembled macrocycles may offer three advantages over macrocycles assembled with transition metals: (1) cheaper starting materials, (2) lower toxicity, and (3) environmental safety. The group of Shea has provided a fundamental start in this area [10]. We report herein our results, in which we connect organic linkages with silicon groups to self-assemble novel macrocycles.

The self-assembly strategy involves the combination of two units that are designed to react with each other

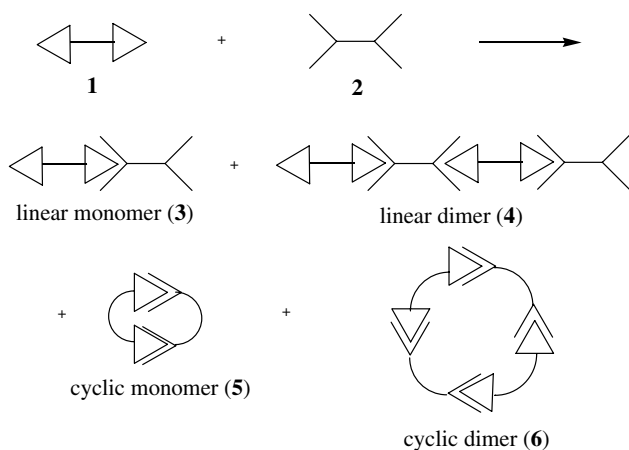
and not with themselves. In the present context, we need to combine an organic ligand capable of reacting in two directions (1 in Scheme 1) with a silicon species (2) able to accept two of these ligands. If the organic ligand and the silicon species react only once, the linear monomer 3 is formed. If the catenation continues with one more of each species, the linear dimer 4 is formed. These linear species are not of interest in this study. If the open ends of the monomer react, the cyclic monomer 5 forms. If the open ends of the dimer react, the cyclic dimer 6 forms. One can similarly imagine the formation of linear and cyclic trimers, tetramers, and so on. Linear and cyclic oligomers may be distinguished by mass spectrometry.

Because of the high strength of the Si–O bond and because of the wide variety of oxygen ligands, we considered only oxygen donors for the organic ligand. Moreover, the presence of two oxygen atoms per donor unit provides double the thermodynamic yield, so that all our organic ligands are bidentate oxygen-chelating reagents. Catechol (7) already has been examined widely as a ligand for silicon [11]. The ability to react



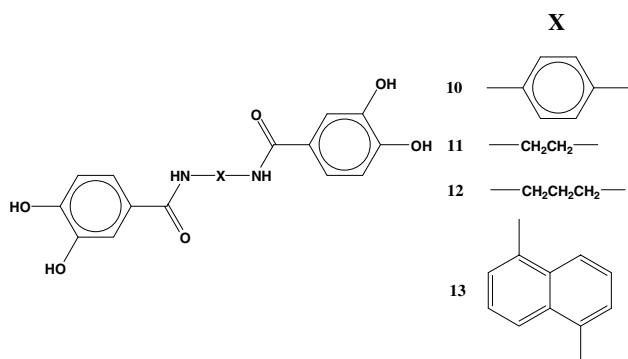
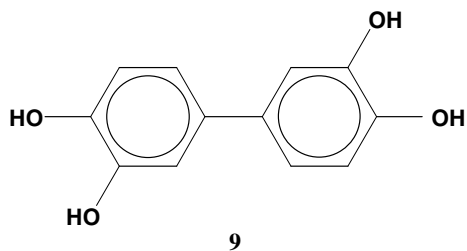
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Scheme 1.

twice to form rings such as **5** and **6** does not refer to this chelation property. Rather, the molecule must double the functionality of catechol and possess two of the *ortho*-dihydroxy linkages. The simplest such molecule is 1,2,4,5-tetrahydroxybenzene (**8**). The nearness of the *ortho*-dihydroxy entities, however, may inhibit ring formation sterically. The functionalities may be made more distant in the biphenyl analogue **9**

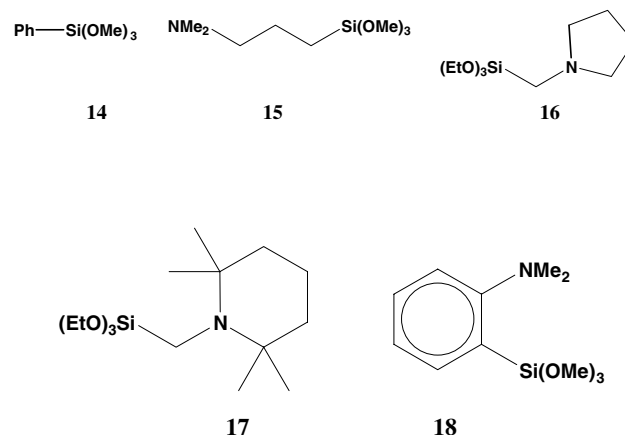


or in the derivatives **10**–**13** studied by Raymond and co-workers [12,13] with other metals. These latter materials are prepared readily by reaction of diamines with derivatized 2,3-dihydroxybenzoic acid.

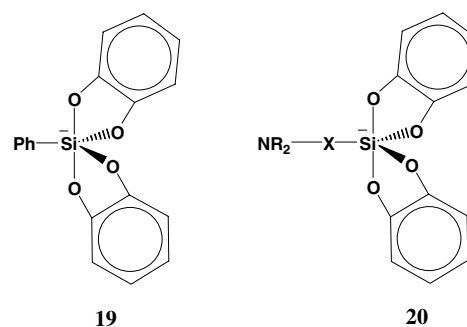
For the silicon molecule in the self-assembling strategy, we decided to use building blocks capable of

hypervalency at silicon. There are several reasons for this decision. (1) A tetravalent silicon would have to react at all four valencies with oxygen (two each from two catechol entities). The resulting silicon is of the silicate or Q variety, in which there is no organic ligand attached through carbon to silicon. Properties may be varied more fully when there is at least one C–Si bond. (2) Bipyramidal, pentacoordinate silicon contains 120° angles in the equatorial plane. Such angles enlarge the distance between groups and reduce steric interactions. It is difficult to predict, however, whether the product would have the trigonal bipyramidal or the square pyramidal geometry. (3) The resulting silicon atoms possess a formal negative charge. The ionic nature may create useful dipolar properties.

Consequently, we selected molecules of the type R–SiX<sub>3</sub> for the silicon part of the self-assembly strategy. We used methoxy and ethoxy as the X leaving groups. After reaction, the three X groups are replaced by two pairs of *ortho*-dihydroxy groups, so that silicon becomes pentavalent and negatively charged. It is unlikely that hexavalent species would be formed because of the higher coulombic charges involved. We have used five such molecules in our study, **14**–**18**. The precise rationale for each of these substrates will become evident in the later discussion.

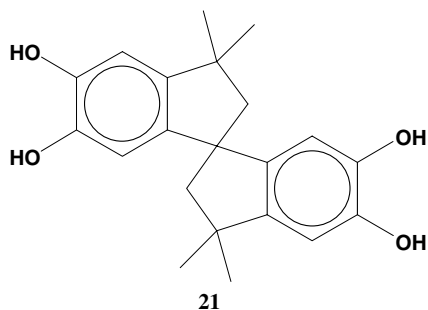


There has been widespread use of catechol as a ligand of pentacoordinate silicon, following the initial preparation of the phenyl derivative **19** by Frye [11].



The crystal structure [14] and many other studies [15–18] followed, with ammonium salts and alkali metals as the accompanying cation, and with both hydroxylic and nonhydroxylic solvents. Tacke and co-workers [19–22] pioneered the use of a fifth substituent that contains an amine group, such as **20**, with the result that, after protonation of nitrogen, the molecule is neutral by charge cancelation. These systems naturally contained no counterion. Tacke obtained crystal structures of several such products, in which the catechol motif had been expanded to include naphthalene and other variations. Geometries ranged from slightly distorted bipyramids to square pyramids. The  $^{29}\text{Si}$  chemical shifts of the catechol complexes varied from  $\delta$  –73.5 to –88.6, with the lower frequency values occurring in systems with more bonds between Si and N [23]. Macrocycles formed from self-neutralizing Tacke ligands would have no overall charge, in contrast to the myriads of charged transition metal macrocycles. Our proposed macrocycle with Tacke ligands thus would have empty cavity space, devoid at least of counterions.

Although numerous studies have been carried out with catechol-like functionalities bound in a bidentate fashion to silicon, very few studies have been reported in which the organic substrate contained two catechol-like functionalities, permitting formation of linear or cyclic oligomers. Raymond and co-workers [12,24–26], examined the reaction of their amide-linked molecules **10–13** with many metals, including gallium and iron, but never with silicon. The only use of silicon as the metal in a dicatechol is found in two studies by Shea and co-workers. They examined the reaction of the simplest such catechol (**8**) with triethoxyphenylsilane in the presence of triethylamine (to neutralize the acid produced and to provide the counterion), but obtained a linear oligomer roughly of the type **4** (but higher oligomerization) with end-group oxidation [27]. The product darkened upon standing in air. They prepared the dicatechol derivative **21** to move the catechol functionalities further apart, to impart an approximately  $90^\circ$  bend via the spiro linkage, to reduce end-group oxidation, and to enhance solubility in organic solvents [10].

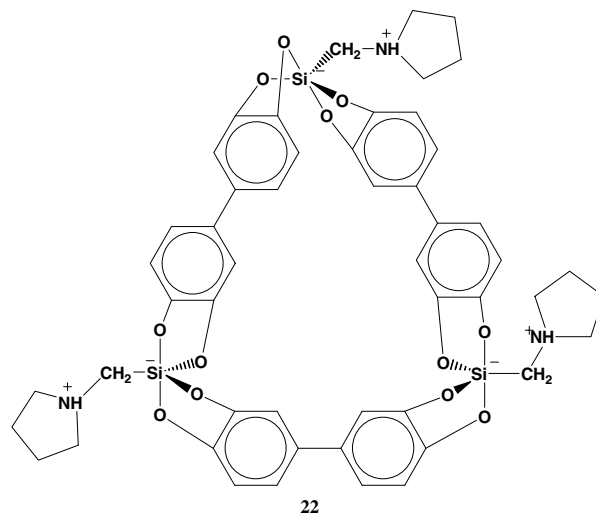


This substrate formed a tetramer (the topological equivalent of a molecular square) on reaction with phenyltriethoxysilane in the presence of triethylamine. Its structure was proved by NMR and MS (no X-ray structures). These investigations have generated four distinct procedures for preparing complexes of catechols with silicon, which we have used throughout our study [10,15,22,28].

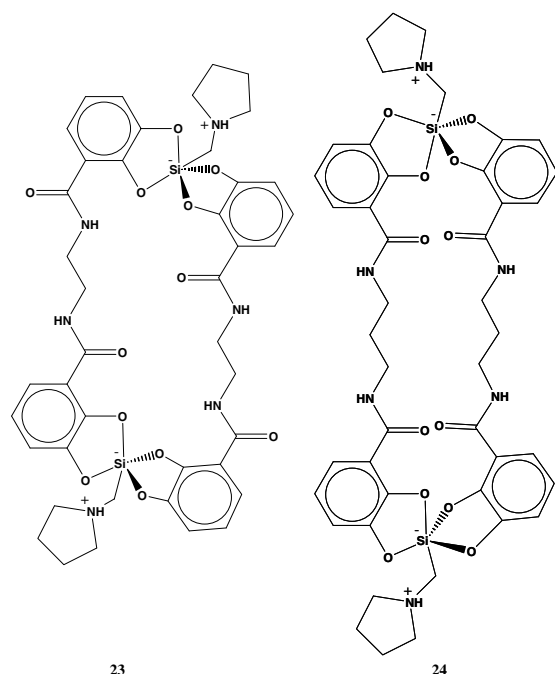
## 2. Results

The various silicon substrates **14–18** were allowed to react with the catechol derivatives **9–13** under a variety of conditions. Only those reactions that successfully yielded cyclic products will be described. The results will be presented according to the catechol derivative.

The only successful reaction of 3,3',4,4'-tetrahydroxybiphenyl (**9**), leading to a cyclic product, occurred with the pyrrolidino substrate **16** in acetonitrile. The reaction produced a high yield of a solid with the exact mass of a cyclic trimer ( $m/z$  980) and a  $^{29}\text{Si}$  chemical shift of  $\delta$  –83.6, indicating a single type of silicon with pentacoordination. Structure **22** suggests the bonding in this molecule but does not depict twisting around the biphenyl bond.



All remaining experiments were carried out with the substrates developed by Raymond, Enemark, and their co-workers [3,13,24–26]. Only limited success was obtained with the catechol derivative containing a bismethylene chain (**11**). On reaction of **11** with pyrrolidino derivative **16** in acetonitrile or tetrahydrofuran (THF), the cyclic monomer ( $m/z$  440) and dimer ( $m/z$  881), according to electrospray MS, were obtained with a  $^{29}\text{Si}$  chemical shift of –84.0. Structure **23** depicts the dimer.



Similar results were obtained with the trimethylene derivative **12** [13]. Reaction with the pyrrolidino derivative **16** in acetonitrile gave the cyclic dimer ( $m/z$  909) (**24**) with a  $^{29}\text{Si}$  resonance at  $\delta$   $-85.3$  but with some minor peaks. Reaction between **12** and **16** in THF gave a solid that showed peaks from monomer, dimer (**24**), and

tetramer in the electrospray mass spectrum (Fig. 1). The large peak at  $m/z$  345 corresponds to fragmentation of the cyclic monomer to produce the ligand **12**, in which three of the phenolic groups are un-ionized (OH) and one is ionized ( $\text{O}^-$ ).

The 1,4-phenylene derivative **10** [13] formed cyclic products with a wider variety of silicon substrates: the monomer ( $m/z$  524) and dimer ( $m/z$  1049) from the *ortho*-phenyl substrate **18** in methanol or THF, the monomer ( $m/z$  491), dimer ( $m/z$  981), and sometimes larger rings from the propyl substrate **15** in methanol or THF, the monomer ( $m/z$  559) and dimer ( $m/z$  1117, **25**) (Fig. 2) with  $^{29}\text{Si}$  chemical shift of

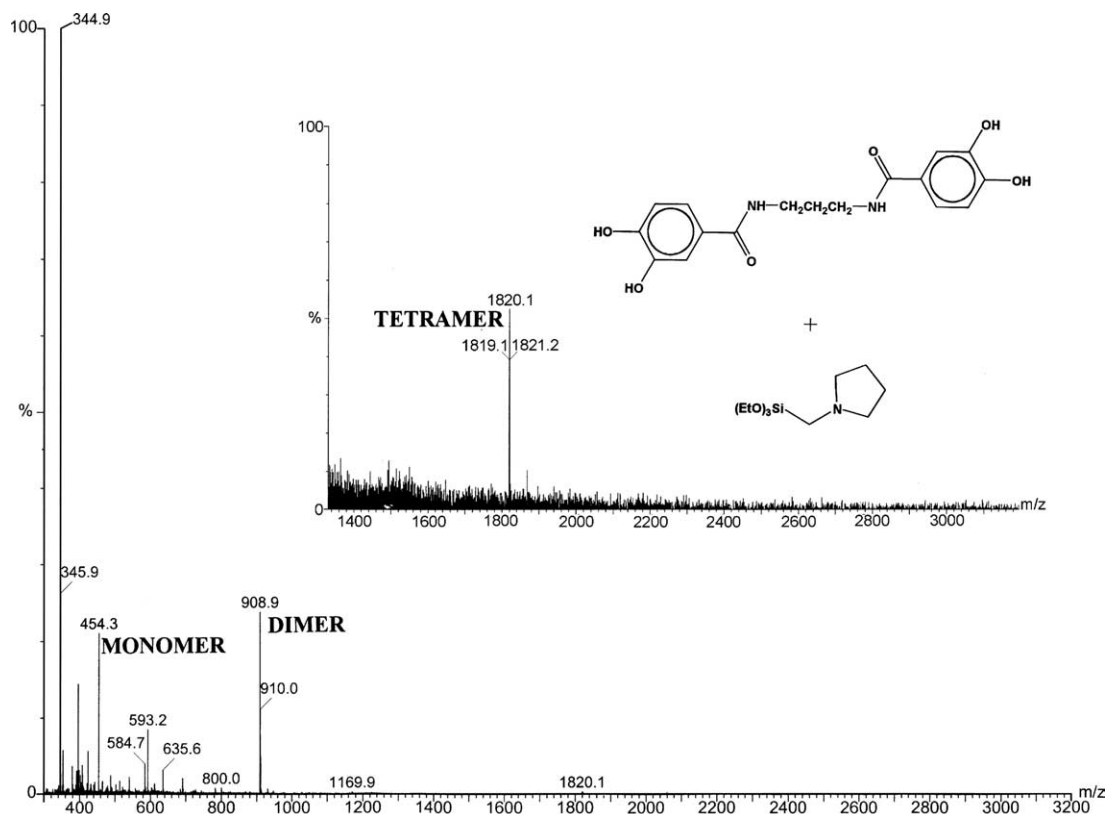
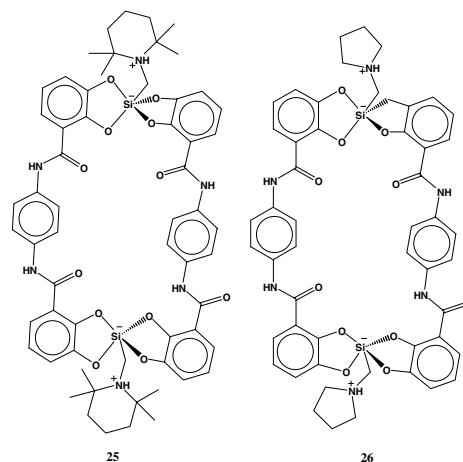


Fig. 1. The electrospray mass spectrum of the products from **12** plus **16**, containing the monomer, dimer (**24**), and tetramer.

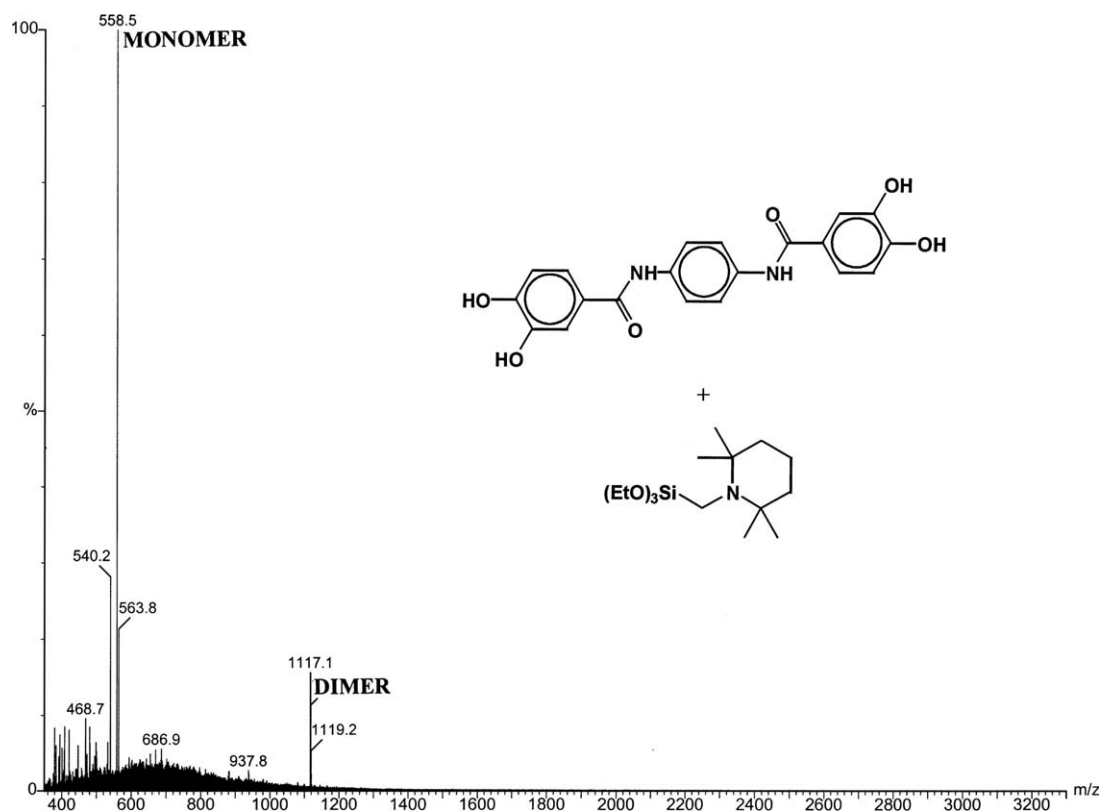
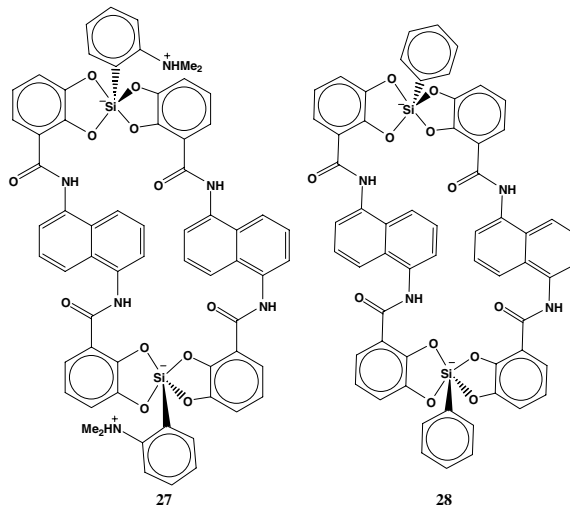


Fig. 2. The electrospray mass spectrum of the products from **10** plus **17**, containing the monomer and dimer (**25**).

$\delta$   $-84.2$  from the piperidino substrate **17** in methanol, and the monomer ( $m/z$  488) and dimer ( $m/z$  977, **26**) (Fig. 3) from the pyrrolidino substrate **16** in methanol or THF. The mass spectrum of **10** plus **17** (Fig. 2) shows the peaks from monomer and dimer (**25**) with little fragmentation. The mass spectrum of **10** plus **16** (Fig. 3) contains the monomer and dimer (**26**), as well as a large peak at  $m/z$  868, most likely from the linear oligomer containing **10** bonded to **16** bonded to **10** with one ionized phenolic hydroxyl. This oligomer could be a mass spectral fragment from the cyclic dimer or, more likely, an original constituent.

The naphthalene derivative **13** [12,13] formed the richest set of cyclic products: the dimer ( $m/z$  1150) (**27**) from the *ortho*-phenyl substrate **18** with  $^{29}\text{Si}$  chemical shift of  $\delta$   $-83.8$  in methanol with base, a mixture of cyclic oligomers from monomer ( $m/z$  575) to pentamer ( $m/z$  2878) from the *ortho*-phenyl substrate **18** in methanol without base (Fig. 4, with peaks primarily from only the cyclic oligomers without fragmentation), the dimer ( $m/z$  1082) with  $^{29}\text{Si}$  chemical shift of  $\delta$   $-73.0$  from the propyl substrate **15** in methanol with base, a mixture of cyclic oligomers from monomer ( $m/z$  541) to pentamer ( $m/z$  2707) from the propyl substrate **15** in methanol without base, the monomer ( $m/z$  608), dimer ( $m/z$  1218), and trimer ( $m/z$  1828) from the piperidino substrate **17** in methanol with base, a mixture of cyclic oligomers from monomer ( $m/z$  609) to tetramer ( $m/z$  2438) with

$^{29}\text{Si}$  chemical shift of  $\delta$   $-84.8$  from the piperidino substrate **17** in methanol without base, the monomer ( $m/z$  539) from the pyrrolidino substrate **16** in methanol with base, a mixture of cyclic oligomers from monomer ( $m/z$  539) to pentamer ( $m/z$  2696) from the pyrrolidino substrate **16** in methanol without base, and the monomer ( $m/z$  532) and dimer ( $m/z$  1063, **28**) (Fig. 5) with  $^{29}\text{Si}$  chemical shift of  $\delta$   $-84.9$  from even the phenyl substrate **14** in methanol with base. The spectrum from **13** plus **14** is exceedingly simple, containing peaks only from the monomer and dimer (**28**).



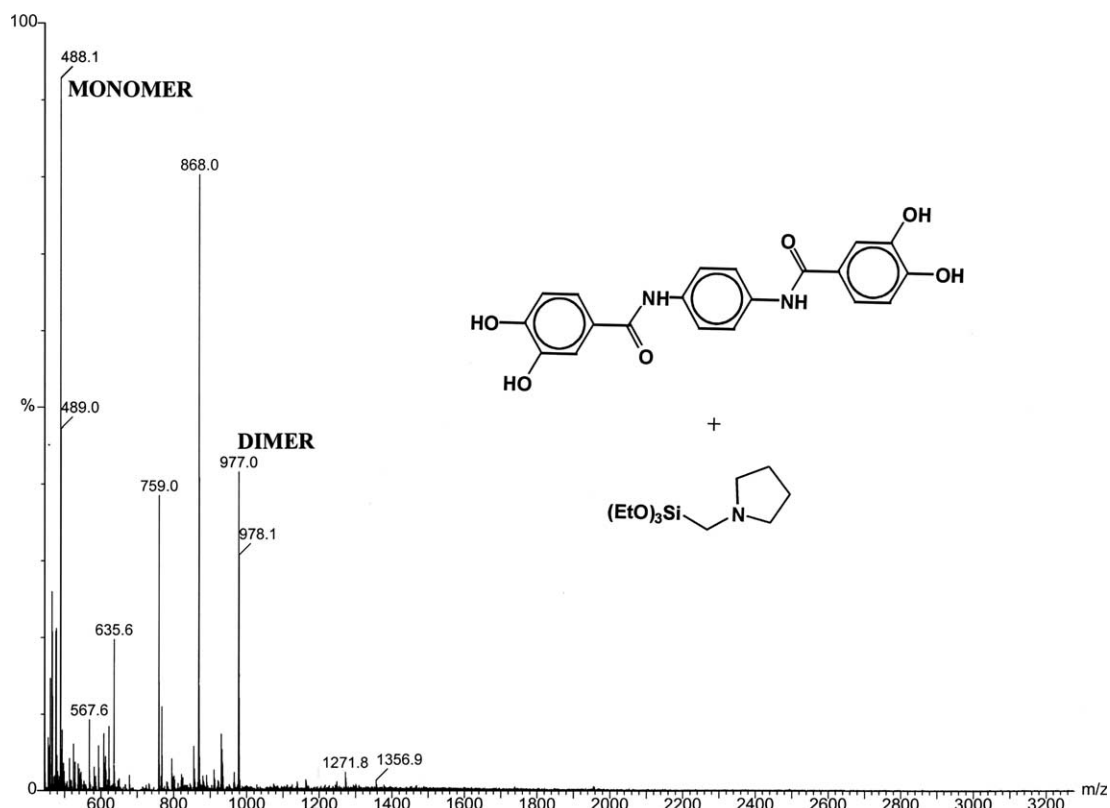


Fig. 3. The electrospray mass spectrum of the products from **10** plus **16**, containing the monomer and dimer (**26**).

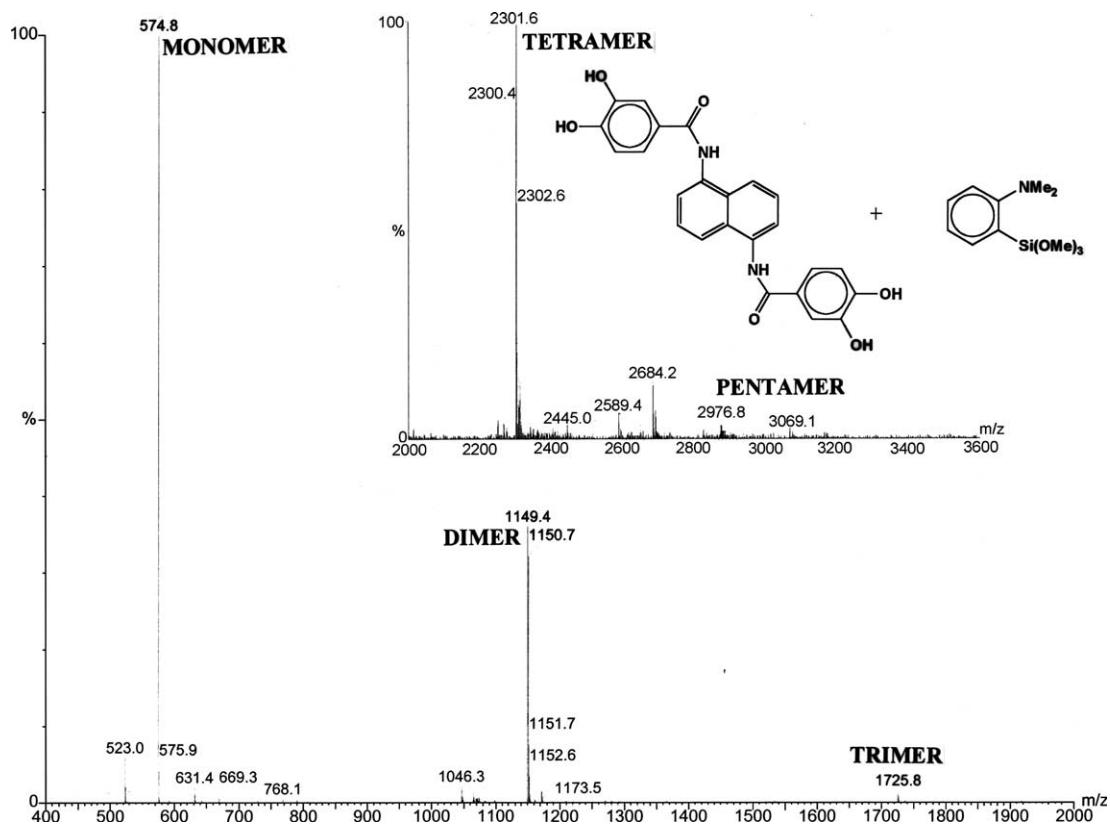


Fig. 4. The electrospray mass spectrum of the products from **13** plus **18**, containing monomer, dimer (**27**), trimer, tetramer, and pentamer.

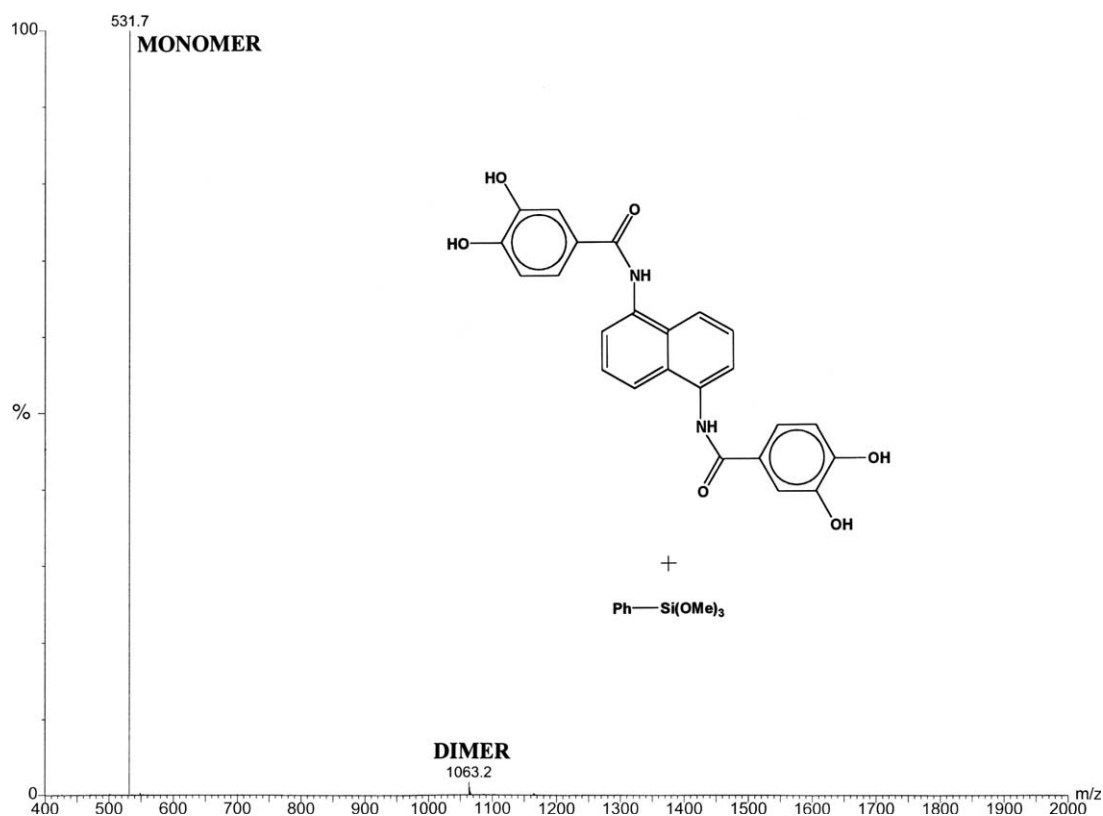


Fig. 5. The electrospray mass spectrum of the products of **13** plus **14**, containing monomer and dimer (**28**).

### 3. Discussion

We examined several variables in determining how to self-assemble macrocycles using pentacoordinate silicon as the metallic linkage: (1) the organic linkage between the two catechol groups, (2) the organic group bonded to silicon (the fifth ligand, as the two catechol groups provide a total of four ligands), and (3) conditions, which included the solvent, the temperature, and the base.

3,3',4,4'-Tetrahydroxybiphenyl (**9**) provides no spacer between the two catechol groups. It failed to produce cyclic oligomers with four out of the five silicon substrates, the one exception being the pyrrolidinomethyl molecule **16**. In almost all cases, however, we did observe linear oligomers, which we did not attempt to characterize. All other organic substrates were based on the bisamide structure. The bismethylene connector between the two amides in **11** was relatively unsuccessful, yielding, like **9**, a cyclic product only with **16**. The trimethylene linkage in **12** was marginally more successful, yielding cyclic products not only with **16** but also with the aminopropyl substrate **15**. The 1,4-phenylene connector between the two amides (**10**) was quite successful, producing cyclic products with all four amino silicon substrates (**15**–**18**). Finally, the 1,8-naphthalene connector **13** reacted successfully with all five silicon substrates.

Size clearly is an important factor, as the smallest connectors (nothing in **9** and the ethylenebisamide in **11**) generally failed, the intermediately sized connectors (propylbisamide **12** and phenylenebisamide **10**) gave mixed results, and the largest connector (naphthalenebisamide **13**) was universally successful. Rigidity also may be important. The flexible saturated connectors **11** and **12** may be too floppy to permit the oligomer ends to meet and react effectively, whereas the rigid connectors **10** and **13** maintain the entire molecule in a reasonably planar geometry that encourages cyclization.

From the point of view of the silicon components, the one containing phenyl as the fourth group (**14**) failed with **9** and achieved success with the naphthaleno organic substrate **13** (it was not tested with **10**–**12**). It would produce highly charged products, a single negative charge arising from each pentacoordinate silicon (one in the monomer, and so on). The other substrates all carry an amino group on the organic chain, after the work of Tacke et al. [19–22] Protonation of the amino nitrogen allows the product to have a net charge of zero and hence require less solvation. We endeavored to enhance solubility by increasing the number of carbon atoms on the fifth substituent. Molecules **17** and **18**, however, must have too much steric hindrance to permit ring formation easily. As a result, molecule **16** proved to be the optimal choice: improved solubility from the carbons, charge neutralization from the amine, and low

steric demands. Although difficult to assess, the distance between the amine and the silicon also may be important, as a shorter distance would tend to enhance coulombic attractions. Molecule **15** has the greatest distance (three carbons) and was generally unsuccessful; molecule **18** has two carbons and steric problems; molecule **17** has one carbon and steric problems. Molecule **16** has one carbon and no steric problem, offering the best situation for both factors.

Higher temperatures tended to favor larger rings. This observation may indicate enthalpic control, if the larger rings are more stable. Entropic control would have favored smaller rings that provide more particles.

For solvents, we examined methanol, octanol, nitromethane, THF, acetonitrile, sulfolane, dimethylsulfoxide (DMSO), dichloromethane, and *N,N'*-dimethylformamide (DMF). Methanol, THF, and acetonitrile proved to be the most successful solvents, although DMSO provided the highest solubility of the products for solution spectra. Although there was no general rule, acetonitrile tended to favor rings over linear oligomers. Methanol tended to produce linear oligomers, possibly by hydrogen bonding to the open ends.

The presence of potassium hydroxide (KOH) in methanol, as used by Raymond and co-workers [3,13,24,25], tended to improve solubility of the starting organic substrates, although the effects of other bases such as triethylamine and sodium bicarbonate also were examined. Generally, without KOH the substrates were introduced in methanol as heterogeneous suspensions. The presence of KOH tended to favor smaller cyclic molecules. The base would deprotonate the hydroxy groups on the organic substrate. Without KOH, larger cyclic oligomers were favored.

We cannot conclude definitively whether we have mixtures of cyclic oligomers in solution or a single higher oligomer that fragments in the mass spectrometer. For the most part, all the oligomers exhibit only a single  $^{29}\text{Si}$  NMR resonance. It is likely, however, that the local structure around silicon does not vary appreciably with oligomer size, so that a single resonance could be found for multiple oligomers. Moreover, it is unlikely that a higher oligomer could extrude one molecule of the organic substrate and one molecule of the silicon substrate, followed by recyclization in the gas phase between chains of very appreciable lengths. Consequently, we prefer the explanation that the solutions contain actual mixtures of oligomers that are validly manifested by the MS analysis. All efforts to separate oligomers by a variety of chromatographic methods failed. The presence of oligomeric mixtures, possibly in equilibrium, doomed all attempts to isolate materials for crystallographic purposes.

In summary, we have prepared and characterized macrocycles containing alternating pentacoordinate silicon and organic struts. The rings vary from monomers

to pentamers. Cyclic oligomers are favored over acyclic oligomers by larger, rigid organic substrates, by silicon substrates containing an amino function and a large number of carbon atoms, and by methanol or acetonitrile as solvent. Larger rings are favored by higher temperatures and by the absence of KOH with methanol as the solvent.

## 4. Experimental

### 4.1. General considerations

3,3',4,4'-Tetrahydroxybiphenyl (**9**) [29,30], *N,N'*-bis(2,3-dihydroxybenzoyl)-1,4-phenylenediamine (**10**) [13], *N,N'*-bis(2,3-dihydroxybenzoyl)ethylenediamine (**11**) [31], *N,N'*-bis(2,3-dihydroxybenzoyl)-1,3-diaminopropane (**12**) [31], *N,N'*-bis(2,3-dihydroxybenzoyl)-1,5-diaminonaphthalene (**13**) [12], triethoxy(pyrrolidinomethyl)silane (**16**) [19,21], triethoxy[(2,2,6,6-tetramethylpiperidino)methyl]silane (**17**) [32], and [2-(dimethylamino)phenyl]trimethoxysilane (**18**) [22] were prepared from literature procedures. Phenyltrimethoxysilane (**14**) (United Chemical Technologies) and [3-(*N,N*-dimethylamino)propyl]trimethoxysilane (**15**) (Gelest) were available commercially. All reactions were performed under nitrogen with anhydrous solvents.

### 4.2. Spectroscopic methods

NMR spectra were recorded on a Varian Mercury 400 ( $^1\text{H}$  at 400 MHz,  $^{13}\text{C}$  at 100 MHz) or a Varian Unity Plus 400 ( $^1\text{H}$  at 400 MHz,  $^{13}\text{C}$  at 100 MHz,  $^{29}\text{Si}$  at 79 MHz) spectrometer under ambient conditions. Mass spectra were generally recorded in the negative-ion electrospray (ES) mode, which results in values that are one unit less than the nominal. Values were rounded off to the nearest whole number, resulting in some round-off error. The reported value is the most intense in the isotopic cluster. Because of the accumulation of  $^{13}\text{C}$  and  $^{29}\text{Si}$  isotopes in the higher molecular weight oligomers, the most intense parent peak moves up from the nominal (based on  $^{12}\text{C}$  and  $^{28}\text{Si}$ ). As a result, reported values for dimers are not necessarily double those of monomers, and so on for higher oligomers.

### 4.3. Reactions between organic and silane substrates

To 3,3',4,4'-tetrahydroxybiphenyl (**9**, 0.20 g, 0.93 mmol) dissolved in  $\text{CH}_3\text{CN}$  (60 mL) was added triethoxy(pyrrolidinomethyl)silane (**16**, 0.23 g, 0.93 mmol) to form a precipitate immediately. The mixture was stirred for 4 days at room temperature, and the precipitate was filtered and washed with  $\text{CH}_3\text{CN}$  to provide 0.41 g of a blue solid (45% based on trimer, **22**):  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  1.9–2.0 (m, 15H), 2.7–2.8 (m, 2H), 6.2 (m, 1H), 6.4



(m, 1H), 6.6–7.0 (m, 2H), 8.9 (br s, 1H);  $^{29}\text{Si}$  NMR (DMSO- $d_6$ )  $\delta$  –83.6; negative-ion ES-MS:  $m/z$  217, 331, 435, 653, 762, 871, 980.

To *N,N'*-bis(2,3-dihydroxybenzoyl)-1,4-phenylenediamine (**10**, 0.20 g, 0.53 mmol) suspended in MeOH (60 mL) was added triethoxy(pyrrolidinomethyl)silane (**16**, 0.13 g, 0.53 mmol) to form a very cloudy mixture immediately. The mixture was stirred for 4 days at room temperature, and the precipitate was filtered and washed with MeOH ( $3 \times 5$  mL) to produce 0.20 g of a white powder (39% based on dimer, **26**):  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  1.8–2.0 (m, 3H), 3.0 (m, 3H), 6.8 (d, 1H), 7.0 (s, 1H), 7.3 (m, 1H), 7.5 (d, 3H), 10.2 (d, 1H); negative-ion ES-MS:  $m/z$  379, 488, 636, 759, 868, 977, 1272, 1357.

To *N,N'*-bis(2,3-dihydroxybenzoyl)-1,4-phenylenediamine (**10**, 0.20 g, 0.53 mmol) dissolved in THF (60 mL) was added triethoxy(pyrrolidinomethyl)silane (**16**, 0.13 g, 0.53 mmol) to form a cloudy, white mixture. The mixture was stirred for 4 days at room temperature, and the precipitate was filtered to afford 0.24 g of a white solid (46% based on dimer, **26**):  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  1.8 (m, 8H), 3.0 (m, 5H), 3.6 (s), 6.8 (m, 2H), 7.0 (m, 2H), 7.3 (m, 2H), 7.5 (d, 4H), 7.7 (s, 1H), 9.1 (br s, 1H), 10.3 (d, 2H); negative-ion ES-MS:  $m/z$  379, 488, 636, 759, 868, 923, 977, 1140, 1249, 1272.

To *N,N'*-bis(2,3-dihydroxybenzoyl)-1,4-phenylenediamine (**10**, 0.20 g, 0.53 mmol) suspended in MeOH (60 mL) was added triethoxy[2,2,6,6-tetramethylpiperidino)methyl]silane (**17**, 0.17 g, 0.53 mmol) to form a slightly less cloudy mixture than before. The mixture was heated at reflux for 4 days (it became very cloudy upon refluxing), and the precipitate was filtered and washed with MeOH ( $3 \times 5$  mL) to give 0.24 g of a white powder (41% based on dimer, **25**):  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  1.1 (m, 8H), 1.3 (m, 8H), 1.5 (m, 5H), 1.7 (m, 5H), 2.9 (m, 3H), 3.2 (m, 2H), 4.1 (m, 1H), 6.4 (br s, 1H), 6.8 (t, 2H), 7.0 (m, 2H), 7.3 (m, 2H), 7.6 (s, 4H), 10.2 (s, 2H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  15, 19, 29, 35, 38, 49, 65, 65, 114, 117, 117, 119, 119, 121, 134, 147, 147, 149, 163;  $^{29}\text{Si}$  NMR (DMSO- $d_6$ )  $\delta$  –84.2; negative-ion ES-MS:  $m/z$  469, 540, 559, 564, 1117.

To *N,N'*-bis(2,3-dihydroxybenzoyl)-1,4-phenylenediamine (**10**, 0.20 g, 0.53 mmol) suspended in MeOH (60 mL) was added [2-(dimethylamino)phenyl]trimethoxysilane (**18**, 0.13 g, 0.53 mmol) to form a cloudy, white mixture. The mixture was stirred for 4 days at room temperature (it became very cloudy after ~15 min), and the precipitate was filtered and washed with MeOH ( $3 \times 5$  mL) to yield 0.20 g of a white powder (36% based on dimer):  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  6.8 (s, 3H), 7.0 (s, 3H), 7.3 (s, 3H), 7.5 (s, 3H), 7.7 (m, 8H), 7.8 (m, 3H), 10.4 (m, 2H); negative-ion ES-MS:  $m/z$  473, 525, 622, 714, 904, 981, 1049, 1071.

To *N,N'*-bis(2,3-dihydroxybenzoyl)-1,4-phenylenediamine (**10**, 0.20 g, 0.53 mmol) dissolved in THF (60 mL) was added [2-(dimethylamino)phenyl]trimethoxysilane

(**18**, 0.13 g, 0.53 mmol). The solution was stirred for 4 days at room temperature (it became cloudy after 2 days), and the precipitate was filtered to produce 0.11 g of a white solid (20% based on dimer):  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  2.6 (s), 6.8 (s, 6H), 7.0 (s, 6H), 7.3 (m, 6H), 7.5 (m, 6H), 7.7 (m, 12H), 7.8–8.0 (m, 12H), 10.2 (m, 1H), 10.4 (m, 6H); negative-ion ES-MS:  $m/z$  490, 524, 593, 759, 795, 855, 870, 920, 1049, 1061, 1095, 1139, 1164, 1175, 1250.

To *N,N'*-bis(2,3-dihydroxybenzoyl)ethylenediamine (**11**, 0.20 g, 0.60 mmol) dissolved in  $\text{CH}_3\text{CN}$  (60 mL) was added triethoxy(pyrrolidinomethyl)silane (**16**, 0.15 g, 0.60 mmol) to form a cloudy, white mixture immediately. The mixture was heated at reflux for 4 days, and the precipitate was filtered and washed with  $\text{CH}_3\text{CN}$  ( $3 \times 5$  mL) to give 0.24 g of a white powder (45% based on dimer, **23**):  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  0.5 (m, 4H), 0.8 (m, 5H), 2.1 (s, 11H), 2.9 (m, 17H), 6.4 (m, 2H), 6.5–6.8 (m, 16H), 6.9–7.0 (m, 5H), 7.2–7.4 (m, 10H), 8.5–8.7 (m, 11H), 9.2 (m, 1H);  $^{29}\text{Si}$  NMR (DMSO- $d_6$ )  $\delta$  –84.0; negative-ion ES-MS:  $m/z$  331, 383, 440, 564, 663, 772, 881, 1019, 1128, 1213, 1337.

To *N,N'*-bis(2,3-dihydroxybenzoyl)-1,3-diaminopropane (**12**, 0.20 g, 0.58 mmol) dissolved in  $\text{CH}_3\text{CN}$  (60 mL) was added triethoxy(pyrrolidinomethyl)silane (**16**, 0.14 g, 0.58 mmol) to form a cloudy, white mixture immediately. The mixture was stirred for 4 days at room temperature, and the precipitate was filtered and washed with  $\text{CH}_3\text{CN}$  ( $3 \times 5$  mL) to afford 0.24 g of a white solid (45% based on dimer, **24**):  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  1.8–1.9 (m, 8H), 2.0 (s, 1H), 3.0 (m, 3H), 3.4 (s), 6.0–6.5 (m, 3H), 6.6–7.0 (m, 5H), 7.1–7.3 (m, 3H), 8.6 (m, 1H), 8.8 (m, 1H);  $^{29}\text{Si}$  NMR (DMSO- $d_6$ )  $\delta$  –84.0, –84.7, –85.3; negative-ion ES-MS:  $m/z$  345, 381, 611, 691, 727, 800, 909.

To *N,N'*-bis(2,3-dihydroxybenzoyl)-1,3-diaminopropane (**12**, 0.20 g, 0.58 mmol) dissolved in THF (60 mL) was added triethoxy(pyrrolidinomethyl)silane (**16**, 0.14 g, 0.58 mmol) to form a cloudy, white mixture. The mixture was heated at reflux for 4 days (it became yellow after 2 h), and the precipitate was filtered to yield 0.20 g of a white solid (38% based on dimer, **24**):  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  1.8–1.9 (m, 10H), 2.8–3.0 (m, 3H), 3.4 (s), 3.6 (s), 6.8 (d, 2H), 6.9 (d, 2H), 7.3 (d, 2H), 8.5 (m), 8.7 (m, 2H), 9.0 (m); negative-ion ES-MS:  $m/z$  345, 454, 593, 909, 1170, 1255, 1820, 1869.

To *N,N'*-bis(2,3-dihydroxybenzoyl)-1,5-diaminonaphthalene (**13**, 0.20 g, 0.47 mmol) suspended in MeOH (60 mL) was added triethylamine (0.13 mL, 0.94 mmol) to form a slightly cloudy solution. Phenyltrimethoxysilane (**14**, 0.13 mL, 0.47 mmol) was added. The solution was heated at reflux for 4 days (it became clear upon refluxing), and the solvent was removed by rotary evaporation to yield 0.29 g of a tan powder (58% based on dimer, **28**):  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  1.1 (t, 35H), 3.0 (m, 21H), 6.8 (t, 7H), 7.0 (t, 10H), 7.3–7.4 (m, 16H), 7.6 (m,

12H), 7.9 (br m, 2H), 10.9 (br s, 2H), 11.3 (br s, 1H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  9, 32, 46, 69, 114, 116, 118, 119, 125, 128, 129, 133, 139, 149, 163;  $^{29}\text{Si}$  NMR (DMSO- $d_6$ )  $\delta$  -84.9; negative-ion ES-MS:  $m/z$  532, 1063.

To *N,N'*-bis(2,3-hydroxybenzoyl)-1,5-diaminonaphthalene (**13**, 0.20 g, 0.47 mmol) suspended in MeOH (400 mL) was added KOH (0.05 g, 0.89 mmol) dissolved in MeOH (2 mL) to produce a clear solution. [2-(Dimethylamino)phenyl]trimethoxysilane (**18**, 0.11 g, 0.47 mmol) was added to give a yellow solution. The solution was stirred for 4 days at room temperature, and the solvent was removed by rotary evaporation to yield 0.35 g of a yellow solid (65% based on dimer, **27**):  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  2.3 (s), 2.6 (m), 2.9 (s), 3.2 (s), 3.5 (s), 6.5 (m, 4H), 6.6 (t, 3H), 6.7–6.9 (m, 18H), 6.9–7.4 (m, 56H), 7.5–7.7 (m, 6H), 8.1 (m, 1H), 8.2 (m, 1H), 10.9–11.1 (m, 8H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  31, 36, 45–46, 49, 112–113, 115–116, 118, 119–120, 122–124, 124–126, 129, 129, 131–132, 133, 136–137, 139, 148, 149, 150, 151–152, 158, 160–161, 162–163, 164–165;  $^{29}\text{Si}$  NMR (DMSO- $d_6$ )  $\delta$  -83.8; negative-ion ES-MS:  $m/z$  429, 479, 508, 569, 609, 677, 862, 1047, 1150, 1189.

To *N,N'*-bis(2,3-dihydroxybenzoyl)-1,5-diaminonaphthalene (**13**, 0.20 g, 0.47 mmol) suspended in MeOH (60 mL) was added [2-(dimethylamino)phenyl]trimethoxysilane (**18**, 0.11 g, 0.47 mmol). The mixture was heated at reflux for 2 weeks, and the precipitate was filtered and washed with MeOH (3  $\times$  5 mL) to afford 0.13 g of a white solid (24% based on dimer, **27**):  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  6.8 (m, 4H), 7.1 (s, 5H), 7.3 (d, 7H), 7.5 (s, 6H), 7.7–7.8 (m, 12H), 8.2 (br s, 2H), 10.1 (br s, 1H), 10.9 (s, 3H); negative-ion ES-MS:  $m/z$  523, 575, 631, 1046, 1150, 1174, 1726, 2302, 2684, 2877.

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