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Molecular Tectonics. Porous Hydrogen-Bonded Networks Built from Derivatives of 9,9′-Spirobifluorene

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Molecules with multiple sites that induce strong directional association tend to form open networks with significant volumes available for the inclusion of guests. Such molecules can be conveniently synthesized by grafting diverse sticky sites onto geometrically suitable cores. The characteristic inability of 9,9′-spirobifluorene to form close-packed crystals suggests that it should serve as a particularly effective core for the elaboration of molecules designed to form highly porous networks. To test this hypothesis, various new tetrasubstituted 9,9′-spirobifluorenes with hydrogen-bonding sites at the 3,3′,6,6′-positions or 2,2′,7,7′-positions were synthesized by multistep routes. Four of these compounds were crystallized, and their structures were determined by X-ray crystallography. In all cases, the compounds form extensively hydrogen-bonded networks with high porosity. In particular, 43% of the volume of crystals of 3,3′,6,6′-tetrahydroxy-9,9′-spirobifluorene (**28**) is available for the inclusion of guests, whereas the porosity is only 28% in crystals of tetrakis(4-hydroxyphenyl)-methane, a close model that lacks the spirobifluorene core. Similarly, the porosities found in crystals of 2,2′,7,7′-tetra(acetamido)-9,9′-spirobifluorene (**33**) and 2,2′,7,7′-tetrasubstituted tetrakis(diaminotriazine) **39** are 33% and 60%, respectively. Moreover, the porosity of crystals of 2,2′,7,7′-tetrasubstituted tetrakis(triaminotriazine) **40** is 75%, the highest value yet observed in crystals built from small molecules. These observations demonstrate that a particularly effective strategy for engineering molecules able to form highly porous networks is to graft multiple sticky sites onto spirobifluorenes or other cores intrinsically resistant to close packing.

Introduction

Learning how to make molecular materials by design is one of the most challenging problems in modern science. Meeting this challenge requires shrewd selection of individual molecular components and artful control of how neighboring molecules are arranged and interact, so that the resulting material has the desired composition, architecture, and properties. Unfortunately, no universal strategy has yet emerged for reaching this ambitious goal.

In the particular field of solid-state chemistry, however, rapid progress in crystal engineering is providing new ways to make predictably ordered molecular materials.[2] An effective strategy in crystal engineering, which has been called molecular tectonics,[3,4] exploits compounds with strong predispositions to associate according to various well-established motifs,[5−12] which have been named supramolecular synthons.[13] The individual associating molecules, called tectons from the Greek word for builder, can be considered to have multiple peripheral sticky sites, which direct molecular association, linked to a core that holds the sticky sites in specific orientations. The core is not merely an anchor point for attaching the sticky sites; it is also an active component that can be chosen judiciously to introduce desirable molecular properties such as luminescence, chirality, catalytic activity, and many others. Because the sticky sites and cores can both be varied widely, molecular tectonics is a potentially powerful tool for creating ordered materials by design.

Crystallization is a complex process of molecular recognition governed by the combined thermodynamic

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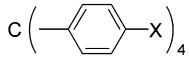
effects of strong directional forces and weak diffuse interactions, as well as by kinetic factors that remain poorly understood.[14] The crystallization of tectons differs from that of normal molecules because specific directional effects are much more important. Like normal molecules, tectons will attempt to form closely packed structures stabilized by weak diffuse interactions; at the same time, however, they must attempt to obey the specific dictates of a small number of strong directional forces. In tectonic association, these forces typically predominate, and close packing is thereby disfavored. Although tectons can be specifically engineered to form close-packed structures in which directional interactions are optimized simultaneously,[7] tectonic association normally leads to the formation of open networks with significant space for the inclusion of guests.

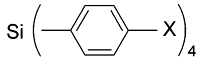
The tendency of tectonic association to favor inclusion is a striking phenomenon of substantial fundamental interest and potential utility. Inclusion typically shows selectivity, and in many cases tectonic networks are robust enough to allow guests to be exchanged in single crystals without loss of crystallinity. Such crystals therefore behave as microporous molecular solids analogous to zeolites, and similar applications in separation, sensing, catalysis, and other areas are being explored. As a result, the control of porosity in ordered molecular materials is a subject of substantial importance. In this paper, we describe an effective strategy for enhancing porosity, and we show how it can be used to make the most porous crystal yet obtained from simple molecular precursors.

Results and Discussion

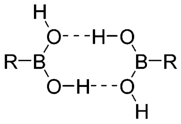
Factors That Help Determine Porosity in Tectonic Networks. Derivatives of tetraphenylmethane (**1**) and tetraphenylsilane (**2**) have been widely used in molecular tectonics because their cores can hold sticky sites in a tetrahedral orientation, allowing diamondoid networks or related three-dimensional, four-connected structures to be created by self-assembly.[15] For example, crystallization of tetraboronic acids **3** and **4** from $CH_3COOC_2H_5$ induces the formation of isostructural diamondoid networks held together by predictable hydrogen bonding, defined by supramolecular synthon **5**.[5] Each diamondoid network is open enough to permit interpenetration by four independent diamondoid networks.[16,17]



1 (X = H)
3 (X = B(OH)$_2$)



2 (X = H)
4 (X = B(OH)$_2$)



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Despite this interpenetration, approximately 60% and 64% of the volume of crystals of tectons **3** and **4**, respectively, is available for including guests.[18,19] These values far exceed those found in crystals of normal molecular analogues such as tetraphenylmethane, tetraphenylsilane, and simple substituted derivatives, which do not typically form inclusion compounds.[20−22] By forming open networks with predetermined architectures, com-

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(18) The percentage of volume accessible to guests was estimated by the PLATON program.[19] PLATON calculates the accessible volume by allowing a spherical probe of variable radius to roll over the internal van der Waals surface of the crystal structure. PLATON uses a default value of 1.20 Å for the radius of the probe, which is an appropriate model for small guests such as water. The van der Waals radii used to define surfaces for these calculations are as follows: C, 1.70 Å; H, 1.20 Å; N, 1.55 Å; O, 1.52 Å; and S, 1.80 Å. If V is the volume of the unit cell and V_g is the guest-accessible volume as calculated by PLATON, then the porosity P in percent is given by $100V_g/V$.

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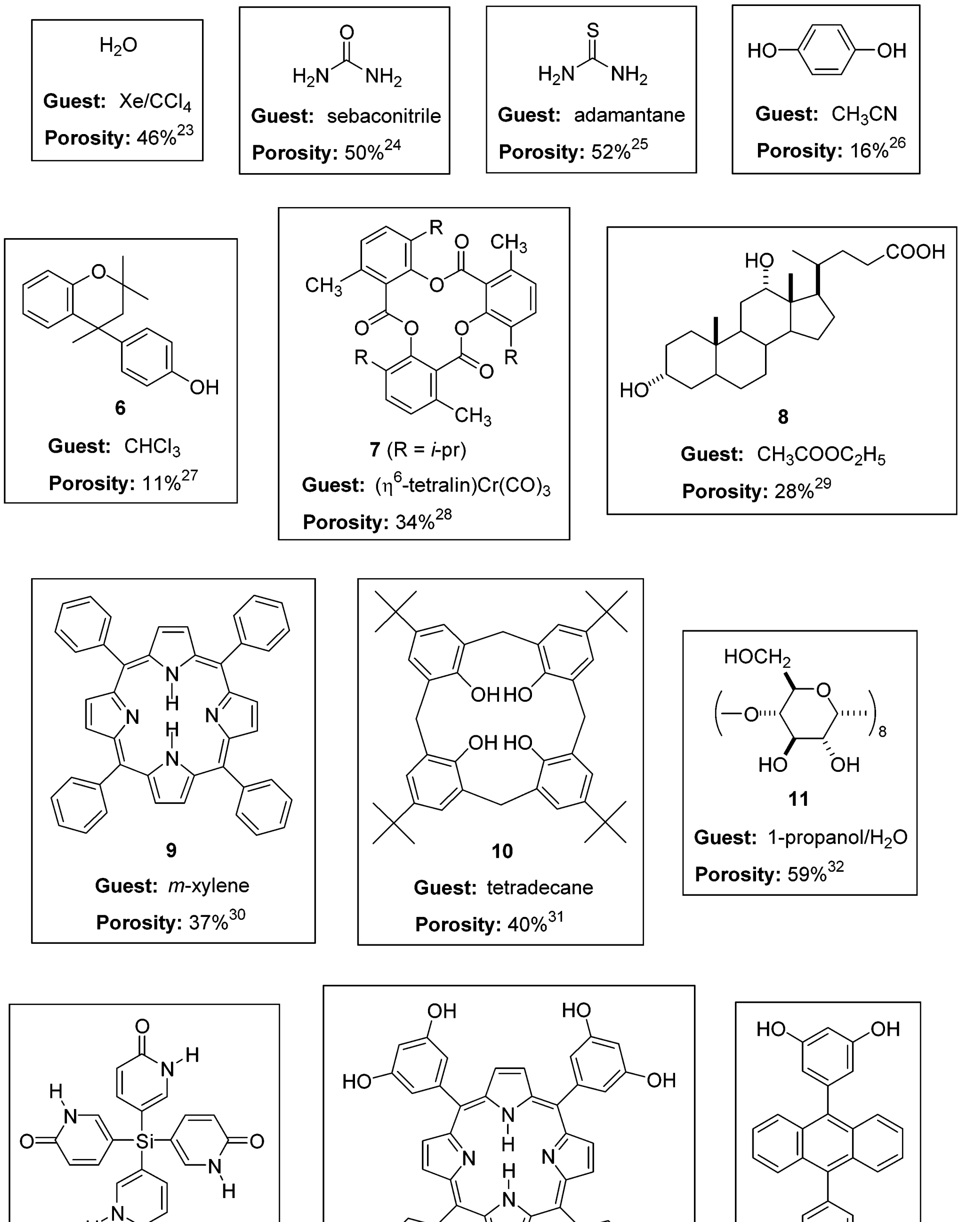
CHART 1. Selected Small Neutral Molecules That Crystallize To Form Families of Inclusion Compounds[a]



[a] The specific guests shown are those for which the porosity, as measured by the percentage of volume accessible to guests,[18] is near the upper limit observed in each family of inclusion compounds.

pounds **3** and **4** show special behavior that supports the emerging principles of molecular tectonics and reveals how profoundly packing in crystals can be changed and controlled by the judicious addition of a small number of sites that take part in strong directional interactions.

To place recent achievements of the field in proper perspective, Chart 1 provides a comparison of the porosity of representative inclusion compounds built from neutral

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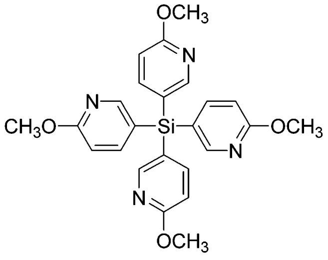
molecules,[10,12,23−33] as measured by the percentage of volume available for guests.[18] Many additional examples, all drawn primarily from the November 2002 version of the Cambridge Structural Database (version 5.24), appear in the Supporting Information. Chart 1 comprises classic families of inclusion compounds, including those formed by water, urea, thiourea, hydroquinone, Dianin's compound (**6**), tri-*ortho*-thymotide (**7**), deoxycholic acid (**8**), 5,10,15,20-tetraphenylporphyrin (**9**), calix[4]arene **10**, and γ-cyclodextrin (**11**). In addition, Chart 1 includes newer compounds **12**−**14**, which have been selected from the recent literature as particularly well-studied examples of small neutral molecules specifically designed to form open hydrogen-bonded networks and to create new families of inclusion compounds. For each molecule in Chart 1, the particular inclusion compound illustrated is one for which the porosity is among the highest observed, so the data in Chart 1 provide an estimate of the upper limits of porosity attained in previously known families of inclusion compounds.

Chart 1 and the further examples in the Supporting Information are not intended to provide a systematic analysis of porosity in molecular solids; nevertheless, the data help set useful guidelines for further research. For example, the porosity of structures assembled from tectons **3**, **4**, **12**, **13**, and **14** (60%, 64%, 65%, 63%, and 62%, respectively) greatly exceeds that of structures formed by models **1**,[21] **2**,[22] **15**,[34] **9**,[30] and **16**,[35] which have similar geometries but lack hydrogen-bonding sites. In all these models the porosities are 0%, except in the case of tetraphenylporphyrin **9** (37%). This comparison confirms that grafting sticky sites to core structures can have a profound effect on packing across a wide range of molecular topologies. In addition, Chart 1 suggests that the highest levels of porosity in hydrogen-bonded networks cannot be attained with small molecules, such as water and urea, presumably because larger molecules tend to have more complex topologies that pack less efficiently in crystals. This accounts for the high percentages of volume often available in protein crystals for the inclusion of water and other guests.[36] Despite the relatively small size and simple symmetric shapes of tectons **3**, **4**, **12**, **13**, and **14**, the porosity of their networks is impressive, even in comparison with that of the most highly porous protein crystals. This is a notable achievement of crystal engineering, and it provides a strong impetus to learn how even higher porosity can be attained.



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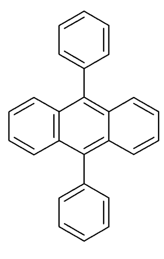

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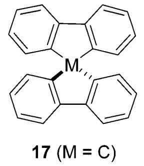
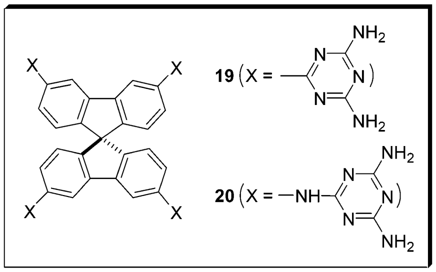
A potential strategy is suggested by the small but significant increase in porosity caused by replacing the central carbon−carbon bonds in tetraboronic acid **3** with longer silicon−carbon bonds in analogue **4**, which places the sticky sites farther from the core. In principle, lengthening the connections between the cores and sticky sites of tectons offers a general strategy for increasing the openness of the resulting networks. Tetraboronic acids **3** and **4** exemplify a case in which this strategy works; in other systems, however, such changes often simultaneously lead to higher degrees of interpenetration, with no net increase in porosity.

An alternative strategy is based on the observation that inclusion compounds of porphyrinic tecton **13** can have exceptional porosities (up to 63%),[12] among the highest values we have been able to find for crystals derived from small neutral molecules. In this case, the high porosity can be attributed in part to the well-known inability of the core itself, 5,10,15,20-tetraphenylporphyrin (**9**), to pack efficiently without including significant numbers of guests.[30,37] Grafting sites for hydrogen bonding onto core **9** then causes further deviations from close packing. This suggests that the search for tectons able to form crystals with significantly higher porosity should focus on targets with core structures intrinsically unable to pack efficiently.

Tectons Derived from Spirobifluorenes. Particularly attractive candidates for new cores are 9,9′-spirobifluorene (**17**) and the analogous silane **18**. Unlike their close relatives tetraphenylmethane and tetraphenylsilane, which form close-packed crystals, spirobifluorenes **17** and **18** are known to form inclusion compounds when



17 (M = C)
18 (M = Si)



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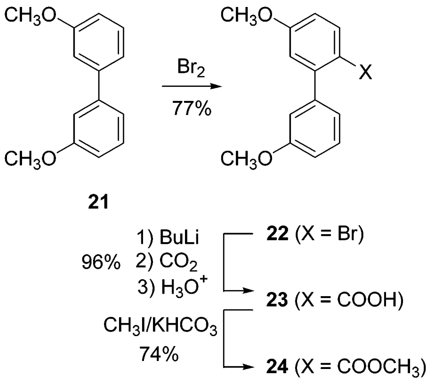
crystallized under diverse conditions.[38,39] In particular, crystallization of silane **18** from tetrahydrofuran yields a structure in which 43% of the volume is available for the inclusion of guests.[39] The markedly different behaviors of tetraphenylmethane and 9,9′-spirobifluorene (**17**), as well as the dissimilarity of the analogous pair of silanes **2** and **18**, can be attributed to the enhanced rigidity of the spirocyclic cores. This prevents rotation of the aryl groups around bonds joining them to the central atom of the core and thereby prohibits conformational changes needed to attain close packing.

For these reasons, replacing tectons derived from tetraphenylmethane and tetraphenylsilane with analogues derived from spirobifluorenes **17** and **18** can be expected to have major effects on packing, possibly leading to new architectures with enhanced porosity and lower levels of interpenetration. Although the 9,9′-spirobifluorene core has been used to create molecular receptors,[40] liquid crystals,[41] polymers,[42] and optical and electronic materials,[43,44] no systematic effort to exploit it in crystal engineering has yet been reported.

Synthesis of Tectons Derived from 3,3′,6,6′-Tetrasubstituted 9,9′-Spirobifluorenes. Derivatives of tetraphenylmethane previously used in crystal engineering have normally been para-substituted, so the synthesis of analogous tectons with sticky sites attached to the 3,3′,6,6′-positions of 9,9′-spirobifluorene was undertaken first. Our principal targets were tectons **19** and **20**, which incorporate four symmetrically located aminotriazine groups. These groups were selected because they can participate in multiple hydrogen bonds according to established motifs, are easily introduced, and have already demonstrated their usefulness in supramolecular chemistry.[6,8] Moreover, the structures of the two analogous tectons derived from tetraphenylmethane are both known,[8,45] allowing potentially illuminating comparisons of architecture and porosity.

Electrophilic substitution of 9,9′-spirobifluorene occurs primarily at the 2,2′,7,7′-positions,[44] so the synthesis of 3,3′,6,6′-tetrasubstituted tectons **19** and **20** required the indirect approach summarized in Schemes 1 and 2. Regioselective monobromination of 3,3′-dimethoxybiphenyl (**21**) gave bromide **22**[46] in 77% yield (Scheme 1).

SCHEME 1



Subsequent lithiation (BuLi), addition of CO_2, and acidification then provided a 96% yield of acid **23**.[46,47] Finally, esterification ($CH_3I/KHCO_3$) gave intermediate **24** in 74% yield.

Dilithiation of 2,2′-dibromo-5,5′-dimethoxybiphenyl (**25**)[48,49] and subsequent addition to ester **24** gave a 50% yield of carbinol **26**, which was transformed under acidic conditions into spirobifluorene **27** in 82% yield (Scheme 2). Deprotection (BBr_3) gave a 91% yield of tetraphenol **28**, which was subsequently converted into triflate **29** in 70% yield. Palladium-catalyzed cyanation with $Zn(CN)_2$ in DMF[50] then gave a 67% yield of tetranitrile **30**, which was converted into target **19** in 72% yield by treatment with dicyandiamide and a catalytic amount of KOH in refluxing 2-methoxyethanol.[51]

The synthesis of tecton **20** required a different approach, outlined in Scheme 3. Regioselective nitration of 9,9′-spirobifluorene (**17**)[44] at the 2,2′,7,7′-positions gave tetranitro derivative **31** in 75% yield. Reduction of the nitro groups gave tetraamine **32** (98%), and subsequent acetylation gave tetraamide **33** (98%), which was again nitrated to give compound **34** in 97% yield. After hydrolysis of the amide groups to give intermediate **35** (96%), reductive deamination[52] gave a 31% yield of tetranitro compound **36**, which was reduced under standard conditions to provide tetraamine **37** in 93% yield. This compound was then converted into target **20** in 62% overall yield by a two-step procedure involving treatment with cyanuric chloride at 0 °C, followed by addition of NH_3.

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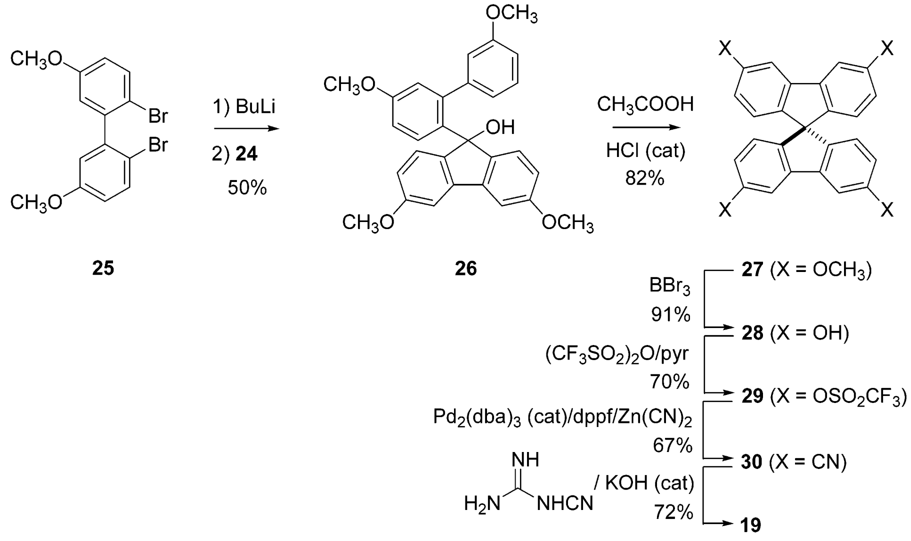
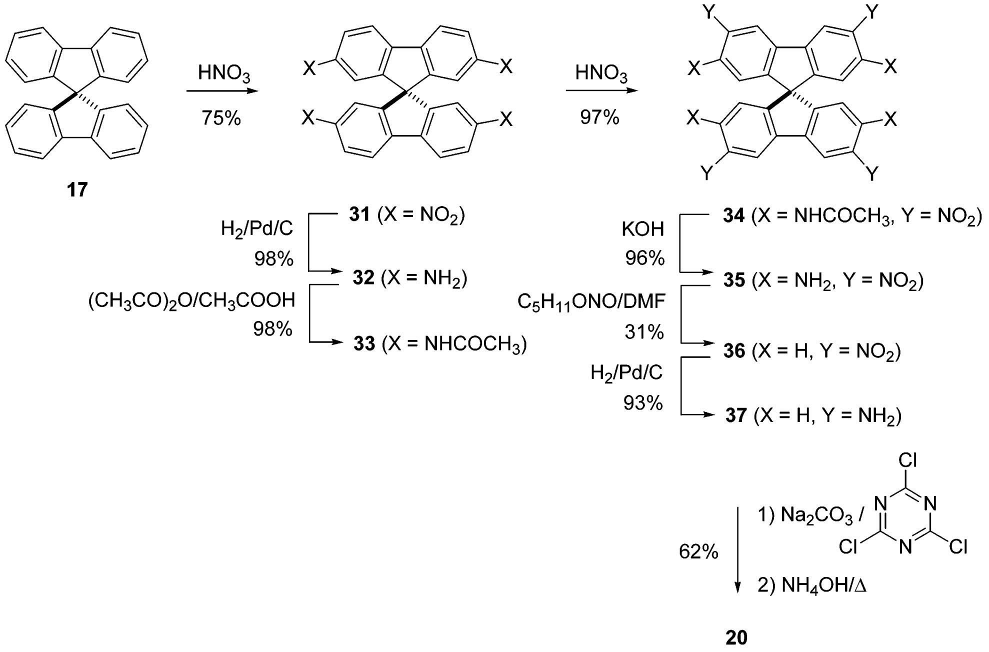
SCHEME 2



SCHEME 3



Structures of Tectons with 3,3′,6,6′-Tetrasubstituted 9,9′-Spirobifluorene Cores. In general, the intermediate spirobifluorenes **27**−**37** have molecular structures that favor self-association and crystallization with inclusion of guests, making all of them worthy candidates for X-ray crystallographic studies. Unfortunately, the compounds of principal interest, tectons **19** and **20**, did not yield crystals suitable for X-ray diffraction, despite multiple attempts to grow them. However, we were able to crystallize 3,3′,6,6′-tetrasubstituted tetraphenol **28** and solve its structure.

Crystals were obtained by diffusion of hexane into solutions of tecton **28** in $CH_3COOC_2H_5$. The crystals belong to the triclinic space group *P*-1 and correspond to an inclusion compound with the composition **28**·$2CH_3COOC_2H_5$. Views of the structure are shown in Figures 1−3. Each molecule of tetraphenol **28** forms hydrogen bonds with three neighboring tectons and with two molecules of $CH_3COOC_2H_5$, as shown in Figure 1. The resulting network is held together by four hydrogen bonds per tecton, and two additional hydrogen bonds per tecton are used to bind the guests. The network is primarily one-dimensional and can be considered to define parallel ladders that are stacked as shown in Figure 2. No hydrogen bonds are formed between individual ladders. The included molecules of $CH_3COOC_2H_5$ occupy parallel channels that have a cross section of approximately 3.6 × 3.2 Å^2 and lie along the *b* axis (Figure 3).[53]

Approximately 43% of the volume of crystals of tetrahydroxyspirobifluorene **28** is available for the inclusion

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[53] The dimensions of a channel in a particular direction correspond to the cross section of an imaginary cylinder that could be passed through the hypothetical open network in the given direction in contact with the van der Waals surface. Such values are inherently conservative because (1) they measure the cross section at the most narrow constriction and (2) they systematically underestimate the sizes of channels that are not uniform and linear.

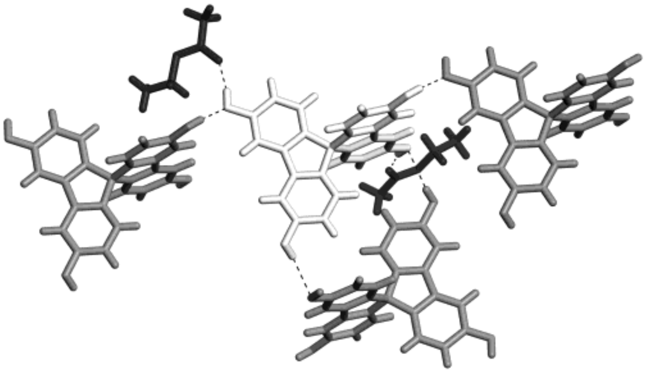


FIGURE 1. View of the structure of 3,3′,6,6′-tetrahydroxy-9,9′-spirobifluorene (**28**) and included $CH_3COOC_2H_5$, showing a central tecton (white) surrounded by its hydrogen-bonded neighbors, which include three other tectons (gray) and two molecules of $CH_3COOC_2H_5$ (black). Hydrogen bonds appear as broken lines. The central tecton (white) uses two of its hydroxyl groups simultaneously as a donor and acceptor of hydrogen bonds to interact with two neighboring tectons and two molecules of $CH_3COOC_2H_5$, and the remaining two hydroxyl groups of the central tecton serve as simple hydrogen-bond donors.

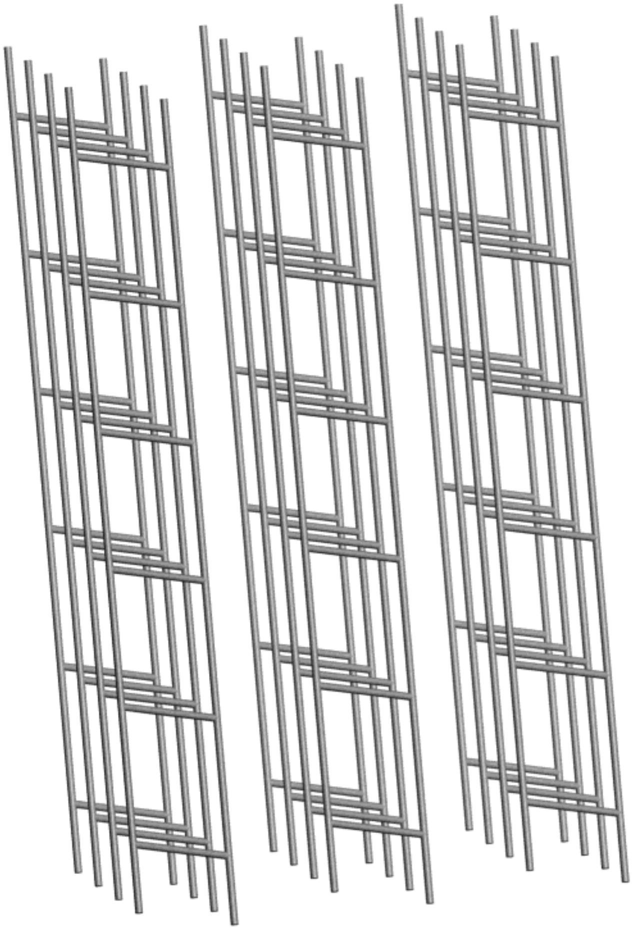


FIGURE 2. Representation of the network generated by the self-association of 3,3′,6,6′-tetrahydroxy-9,9′-spirobifluorene (**28**). In this drawing, the central spirocyclic carbon atoms of the tectons are considered to lie at the intersections of the solid lines, and the lines themselves connect the center of each tecton with the centers of its three hydrogen-bonded neighbors.

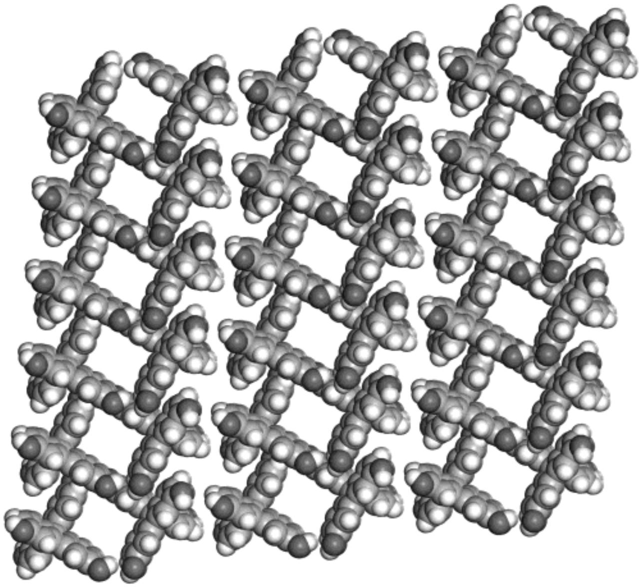
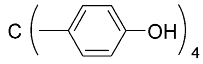


FIGURE 3. View along the *b* axis of the network constructed from 3,3′,6,6′-tetrahydroxy-9,9′-spirobifluorene (**28**) showing a 6 × 2 × 3 array of unit cells. Guests are omitted, and atoms are shown as spheres of van der Waals radii in order to reveal the cross sections of the channels. Atoms of hydrogen appear in white, atoms of carbon in light gray, and atoms of oxygen in dark gray.

of guests.[18] Although this porosity is modest by current standards, it is significantly higher than that of crystals of a very close relative, tetrakis(4-hydroxyphenyl)methane (**38**), when grown under identical conditions



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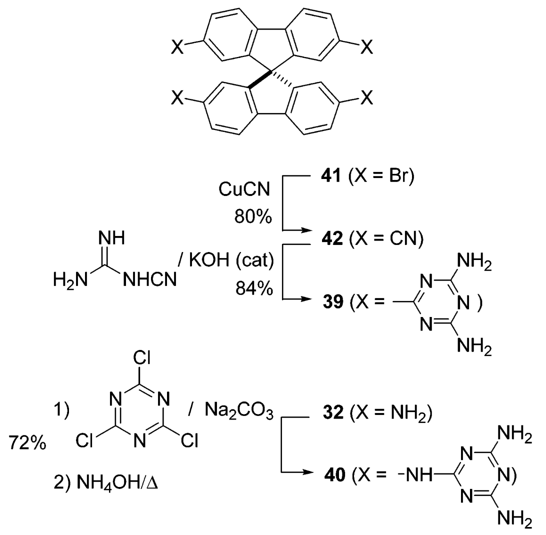
(28%).[7] Detailed comparison of the two structures clearly reveals the major effects that replacing a tetraphenylmethane core by a spirobifluorene core can have in molecular tectonics. In particular, spirobifluorene **28** forms an inclusion compound with stoichiometry **28**·$2CH_3COOC_2H_5$, whereas the analogous tetraphenylmethane **38** yields crystals with composition **38**·$CH_3COOC_2H_5$. Moreover, spirobifluorene **28** has fewer hydrogen-bonded neighboring tectons (three) than does the closely related tetraphenylmethane **38** (four). Together, these observations confirm that the characteristic rigidity and topology of the spirobifluorene core can be used to good effect in molecular tectonics to produce crystals (1) with greater porosity than that found in crystals built from analogous tetraphenylmethanes and (2) with structures in which each tecton has a smaller number of hydrogen-bonded neighbors. As a result, we were encouraged to continue exploring the consequences of attaching sites for hydrogen bonding to the spirobifluorene core.

Synthesis of Tectons Derived from 2,2′,7,7′-Tetrasubstituted 9,9′-Spirobifluorenes. Because 2,2′,7,7′-tetrasubstituted derivatives of 9,9′-spirobifluorene are readily accessible by direct electrophilic substitution of 9,9′-spirobifluorene, we decided to undertake the synthesis of tectons **39** and **40** according to the route

SCHEME 4



summarized in Scheme 4. The reaction of CuCN[54] with the known tetrabromospirobifluorene **41**[44] afforded tetranitrile **42** in 80% yield. Conversion to tecton **39** was accomplished in 84% yield by treatment with dicyandiamide and a catalytic amount of KOH.[51] Tecton **40** was made from tetraamine **32** (Scheme 3) in 72% overall yield by reaction with cyanuric chloride followed by aminolysis. Unlike 3,3′,6,6′-tetrasubstituted tectons **19** and **20**, 2,2′,7,7′-tetrasubstituted isomers **39** and **40** both gave crystals suitable for X-ray analysis, as did 2,2′,7,7′-tetrasubstituted tetraacetamide **33** (Scheme 3).

Structures of Tectons with 2,2′,7,7′-Tetrasubstituted 9,9′-Spirobifluorene Cores. Crystals of tetraamide **33** were grown from acetone/DMF and were found to belong to the monoclinic space group $C2/c$ and to have the composition **33**·$2CH_3COCH_3$. Self-association produces the extensively hydrogen-bonded network shown in Figure 4. The included acetone is ordered but does not form hydrogen bonds with the network. Each tecton participates in a total of eight hydrogen bonds with six neighboring tectons, of which only three are shown in Figure 4. The resulting network defines parallel channels that have no significant connections, and the included molecules of acetone lie in these channels. Approximately 33% of the volume is available for the inclusion of guests,[18] confirming again the suitability of the spirobifluorene core for engineering porous crystals.

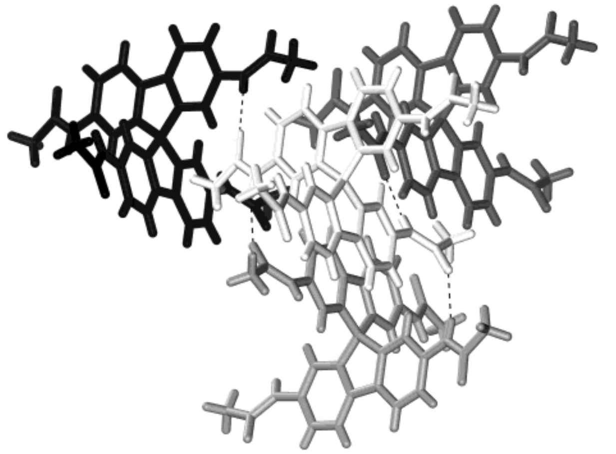


FIGURE 4. Representation of the structure of crystals of tetraacetamide **33** grown from acetone/DMF, showing a tecton (white) surrounded by three of a total of six hydrogen-bonded neighboring tectons. The other three neighbors are equivalent by symmetry and are omitted for clarity, as are included molecules of acetone. Hydrogen bonds appear as broken lines. Each acetamido group serves simultaneously as a donor and acceptor of hydrogen bonds. Two neighbors (one shown in light gray, with a second equivalent by symmetry and omitted) each accept one hydrogen bond and donate another, two other neighbors (dark gray) each accept a single hydrogen bond, and the final two neighbors (black) each donate a single hydrogen bond.

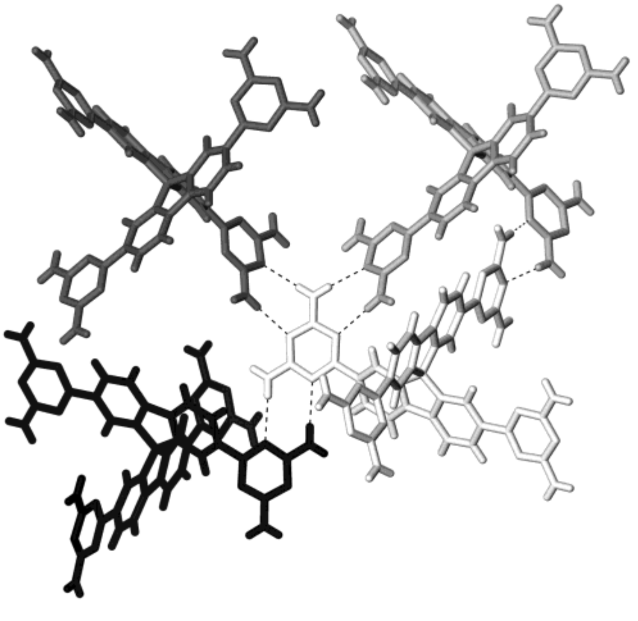


FIGURE 5. Representation of the structure of crystals of tetrakis(diaminotriazine) **39** grown from DMSO/dioxane, showing a tecton (white) surrounded by three of a total of six hydrogen-bonded neighboring tectons. The other three neighbors are equivalent by symmetry and are omitted for clarity, as are all guests. Hydrogen bonds appear as broken lines. Two of the six neighbors (one shown in dark gray, with a second equivalent by symmetry and omitted) each form two hydrogen bonds with the central tecton (white), creating motifs of type **43**. Two other neighbors (light gray) each form four hydrogen bonds with the central tecton, creating distorted motifs of type **44**, and the remaining two neighbors (black) each form two hydrogen bonds with the central tecton according to motif **45**.

Crystallization of the 2,2′,7,7′-tetrasubstituted tetrakis(diaminotriazine) **39** from DMSO/dioxane gave an inclusion compound of approximate composition **39**·4DMSO·7dioxane·$x$$H_2O$,[55] and the structure was determined by X-ray diffraction. Views of the structure are shown in Figures 5 and 6. As expected, tecton **39** self-associates by hydrogen bonding of the diaminotriazine groups, thereby forming an open three-dimensional network. The resulting network has significant space for both interpenetration and inclusion of guest molecules. Each tecton participates in a total of 16 hydrogen bonds with six neighbors, creating the assembly shown in Figure 5. As

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(55) The composition was estimated by X-ray crystallography and by ^1H NMR spectroscopy of dissolved samples. The amount of included H_2O could not be determined accurately.

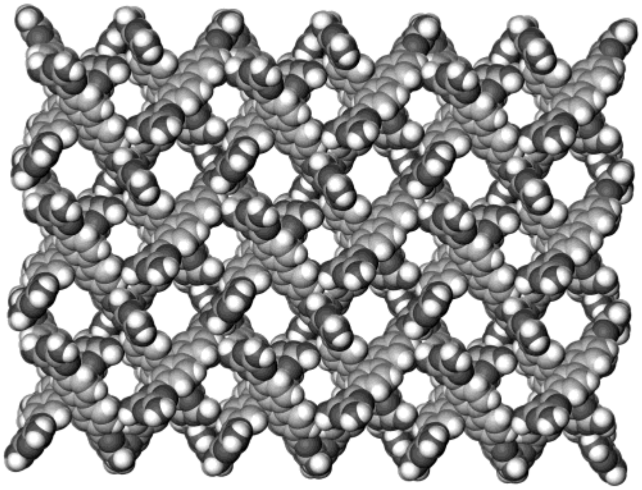


FIGURE 6. View along the *a* axis of the network constructed from tecton **39** showing a $2 \times 3 \times 3$ array of unit cells. Guests are omitted, and atoms are shown as spheres of van der Waals radii in order to reveal the cross sections of the channels. Atoms of hydrogen appear in white, atoms of carbon in light gray, and atoms of nitrogen in dark gray.

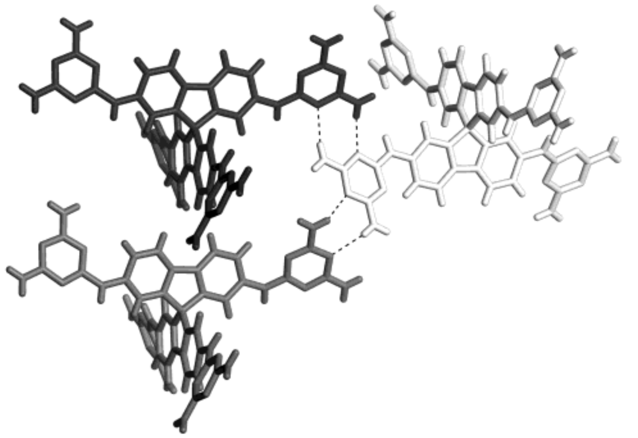
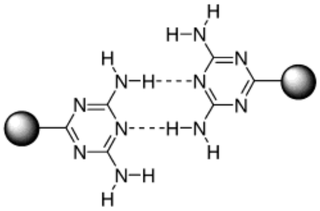


FIGURE 7. Representation of the structure of crystals of tetrakis(triaminotriazine) **40** grown from DMSO/dioxane, showing a tecton (white) surrounded by two of a total of eight hydrogen-bonded neighboring tectons (dark gray and black). Each of the two illustrated neighbors is equivalent by symmetry to three others, which are omitted for clarity, as are all guests. Hydrogen bonds appear as broken lines. The central tecton (white) shares two hydrogen bonds with each neighboring tecton according to motif **43** (dark gray) or motif **45** (black).

previously observed in other networks constructed from diaminotriazines,[6] hydrogen bonding occurs according to motifs **43**−**45**. Motif **43** involves the more accessible N-3/N-3′ nitrogen atoms and is therefore expected to be stronger than the alternative N-1/N-3′ and N-1/N-1′ motifs **44** and **45**. In the network built from tecton **39**, two of the six neighbors each form two hydrogen bonds with the central tecton according to motif **43**. In this case, the spirocyclic centers of the central tecton and each neighbor are separated by 15.4 Å. Together, the tectons that interact in this way define square grids that are stacked in parallel along the *c* axis. Two other neighbors each form four hydrogen bonds with the central tecton, creating distorted motifs of type **44**. In this case, the intertectonic distances are 11.6 Å. The remaining two neighbors are separated from the central tecton by 15.3 Å, and each forms two hydrogen bonds with the central tecton according to motif **45**. Together, the central tecton and the four neighbors that interact according to motifs **44** and **45** define a diamondoid network with 2-fold interpenetration. The complex interpenetration of diamondoid and square planar networks may arise because the intertectonic separation is too small to permit 3-fold diamondoid interpenetration, yet too large to prevent the incorporation of another type of network.



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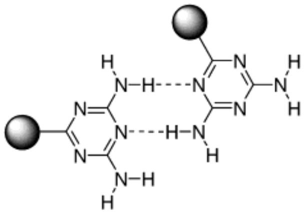

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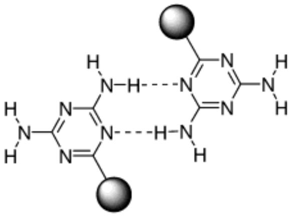

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Despite the presence of multiple interpenetrating networks, nearly 60% of the volume of crystals built from tecton **39** remains available for the inclusion of guests.[18] The guests are highly disordered and lie in two types of channels aligned with the *a* axis (Figure 6). The cross sections of these channels measure approximately 4.2×4.2 Å^2 and 3.9×3.9 Å^2 at the narrowest points.[53] The behavior of tecton **39** provides further evidence that attaching multiple hydrogen-bonding sites to the spirobifluorene core is an effective strategy for creating molecules predisposed to form highly porous crystals.

Even higher porosity was found in crystals of the 2,2′,7,7′-tetrasubstituted tetrakis(triaminotriazine) **40**, which were grown from DMSO/dioxane. The crystals proved to belong to the tetragonal space group *P*-4*b*2 and to have the approximate composition **40**·8DMSO·8dioxane·xH$_2$O.[55] Views of the structure are shown in Figures 7−10. The triaminotriazine groups associate extensively according to hydrogen-bonding motifs **43** and **45**, thereby generating a network in which each tecton forms a total of 16 hydrogen bonds with eight symmetrically oriented neighboring tectons (Figure 7). Each triaminotriazine group participates in two hydrogen bonds of type **43** with one set of four neighbors that are equivalent by symmetry (dark gray), and each triaminotriazine group also forms two other hydrogen bonds according to motif **45** with a second set of four equivalent neighbors (black). The tectons linked by motif **43** define a 4-fold interpenetrated diamondoid network (Figure 8), whereas those joined by motif **45** generate a square planar network.

Despite this complex interpenetration, the resulting structure contains impressive channels parallel to the *c* axis (Figures 9 and 10). Their cross section (Figure 9) measures approximately 13×13 Å^2,[53] and the channels themselves are represented by the surface shown in Figure 10.[56] This view establishes that the channels have

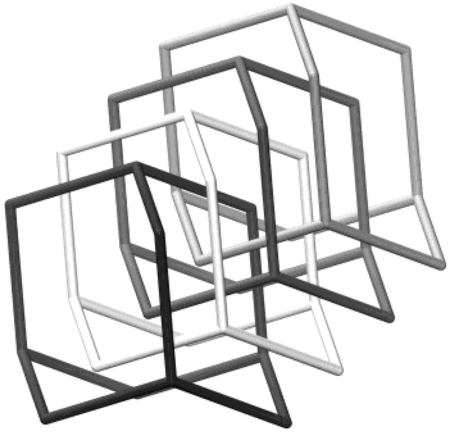

FIGURE 8. Representation of the 4-fold interpenetrated diamondoid networks generated by association of tecton **40**. In this drawing, the central spirocyclic carbon atom of each tecton lies at the intersections of solid lines that represent hydrogen bonding to four neighbors according to motif **43**. The independent networks are shown in different shades of gray.

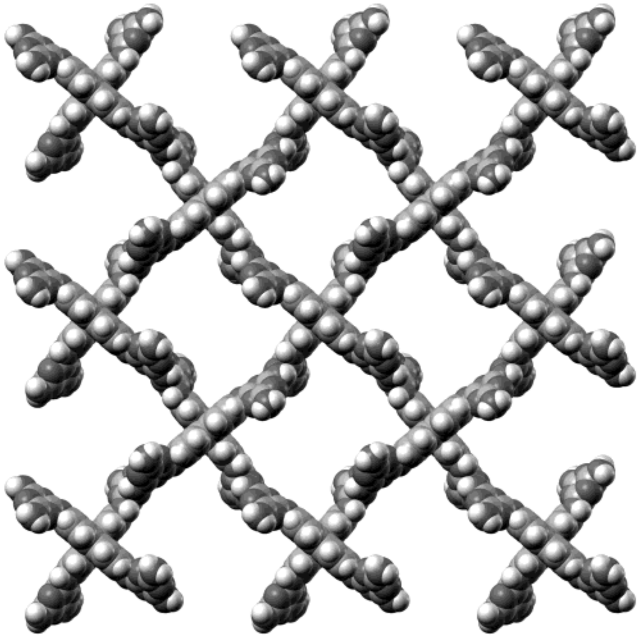

FIGURE 9. View along the *c* axis of the network constructed from tecton **40** showing a 2 × 2 × 4 array of unit cells. Guests are omitted, and atoms are shown as spheres of van der Waals radii in order to reveal the cross sections of the channels. Atoms of hydrogen appear in white, atoms of carbon in light gray, and atoms of nitrogen in dark gray.

an irregular helical shape with no significant interconnections; although the individual channels are chiral, equal numbers of helices of opposite handedness are present. Fully 75% of the volume of the crystals remains available for the inclusion of guests.[18] To our knowledge, the porosity of this system is the highest ever reported for a crystal built from small molecules.

Conclusions

The detailed structures of molecular crystals cannot yet be predicted with accuracy,[57] but research in crystal engineering is providing increasingly powerful tools for designing molecules that are predisposed to form structures with particular features. Especially rapid progress has been made in learning how to make molecular crystals in which significant volume is available for the inclusion of guests. A particularly promising strategy for making porous crystals is to build them from molecules that interact with their neighbors by strongly directional forces, thereby disfavoring close packing and leading to the formation of open networks. Such molecules can be made conveniently by grafting sticky sites onto suitable cores. If the cores are chosen to have topologies that make efficient packing inherently impossible, then the resulting molecules should yield especially porous crystals. This hypothesis is supported by the behavior of tectons **28**, **33**, **39**, and **40**, in which multiple sites for hydrogen bonding are attached to a spirobifluorene core. In particular, crystals of tecton **40** have a porosity of 75%, the highest value ever reported for a crystal built from small molecules. We are optimistic that this strategy can be exploited to make molecular crystals with even higher porosity and useful applications in separation, catalysis, and other areas.

Experimental Section

2-Bromo-3′,5-dimethoxy-[1,1′-biphenyl] (22).[46] A solution of 3,3′-dimethoxy-[1,1′-biphenyl] (**21**; 12.7 g, 59.3 mmol) in CCl_4 (70 mL) was stirred at 0 °C and treated dropwise with a solution of Br_2 (3.3 mL, 64 mmol) in CCl_4 (20 mL). The resulting mixture was stirred at 25 °C for 1.5 h, and then saturated aqueous $Na_2S_2O_3$ was added (50 mL). The mixture was extracted with CH_2Cl_2, and the organic phase was washed with water and brine, dried over $MgSO_4$, and filtered. Volatiles were removed by evaporation under reduced pressure, and the resulting oil was purified by flash chromatography (silica, toluene (80%)/ether (20%)) to afford 2-bromo-3′,5-dimethoxy-[1,1′-biphenyl] (**22**; 13.3 g, 45.4 mmol, 77%)[46] as a colorless oil: IR (film, NaCl) 1590, 1566, 1464, 1232, 1031 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 1H, $^3J = 8.8$ Hz), 7.37 (t, 1H, $^3J = 7.7$ Hz), 7.03−6.95 (m, 3H), 6.92 (d, 1H, $^4J = 3.1$ Hz), 6.81 (dd, 1H, $^3J = 8.8$ Hz, $^4J = 3.1$ Hz), 3.87 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 159.2, 143.7, 142.9, 134.1, 129.4, 122.1, 117.0, 115.4, 115.2, 113.7, 113.4, 55.9, 55.7; MS (EI+) 292; HRMS (EI+) calcd for $C_{14}H_{13}BrO_2$ *m/e* 292.009891, found 292.009680.

3′,5-Dimethoxy-[1,1′-biphenyl]-2-carboxylic Acid (23).[46,47] A solution of 2-bromo-3′,5-dimethoxy-[1,1′-biphenyl] (**22**; 13.3 g, 45.4 mmol)[46] in diethyl ether (400 mL) was stirred at −10 °C under dry N_2 and treated dropwise with a solution of butyllithium (25 mL, 2.5 M in hexane, 62 mmol). After 15 min, gaseous CO_2 was bubbled through the mixture, and the temperature was allowed to rise to 25 °C. The resulting mixture was acidified with aqueous 1 M HCl and extracted with diethyl ether. The organic phase was washed with water and brine, dried over $MgSO_4$, and filtered. Volatiles were removed by evaporation under reduced pressure, and the residue was crystallized from acetone/pentane to afford 3′,5-dimethoxy-[1,1′-biphenyl]-2-carboxylic acid (**23**; 11.3 g, 43.8 mmol, 96%)[46,47] as a light yellow solid: mp 126−128 °C (lit.[47] mp 126−128 °C); IR (KBr) 3200−2400, 1692, 1666, 1600, 1566,

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(56) Representations of channels were generated by the Cavities option in the program ATOMS (*ATOMS*, version 5.1; Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663; www.shapesoftware.com). We are grateful to Eric Dowty of Shape Software for integrating this capacity in ATOMS at our suggestion.

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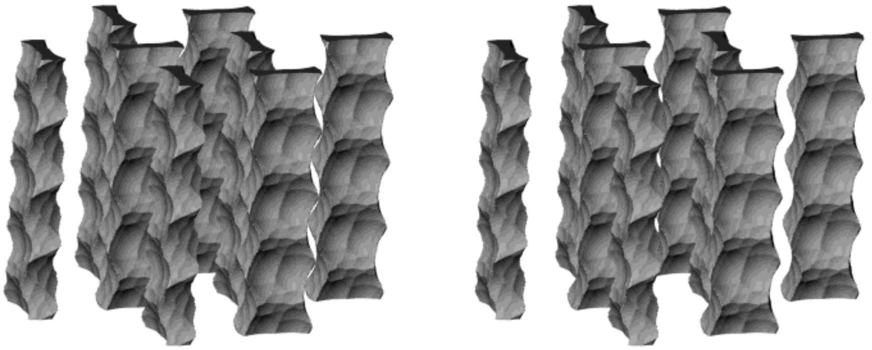

FIGURE 10. Stereoscopic representation of the parallel helical channels defined by the network constructed from tecton **40**. The image shows a 2 × 2 × 4 array of unit cells viewed with the *c* axis vertical. The outsides of the channels appear in light gray, and dark gray is used to show where the channels are cut by the boundaries of the array. The surface of the channels is defined by the possible loci of the center of a sphere of diameter 7 Å as it rolls over the surface of the ordered tectonic network.[56]

1452, 1436, 1294, 1282, 1224, 1023 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, 1H, ^3J = 8.7 Hz), 7.30 (t, 1H, ^3J = 8.0 Hz), 6.94−6.87 (m, 4H), 6.84 (d, 1H, ^4J = 2.6 Hz), 3.87 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100.1 MHz, CD_3OD) δ 170.6, 162.2, 159.7, 145.4, 143.4, 132.3, 128.9, 123.6, 120.9, 116.4, 114.2, 112.7, 112.3, 55.0, 54.7; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 258. Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.58; H, 5.49.

Methyl 3′,5-Dimethoxy-[1,1′ -biphenyl]-2-carboxylate (24). A solution of 3′,5-dimethoxy-[1,1′-biphenyl]-2-carboxylic acid (**23**; 11.3 g, 43.8 mmol)[46,47] in anhydrous DMF (100 mL) was treated with $KHCO_3$ (11.5 g, 115 mmol). The mixture was stirred at 25 °C and treated dropwise with CH_3I (7.0 mL, 110 mmol). After 24 h, the mixture was diluted with water (200 mL) and extracted with diethyl ether (3 × 100 mL). The organic phase was washed thoroughly with water (5 × 100 mL) and brine (100 mL), dried over $MgSO_4$, and filtered. Volatiles were removed by evaporation under reduced pressure, and the residue was purified by flash chromatography (silica, $CH_3COOC_2H_5$ (15%)/hexane (85%)) to afford methyl 3′,5-dimethoxy-[1,1′-biphenyl]-2-carboxylate (**24**; 8.76 g, 32.2 mmol, 74%) as a colorless oil: IR (film, NaCl) 1718, 1600, 1568, 1484, 1464, 1434, 1286, 1255, 1236, 1038 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, 1H, ^3J = 8.6 Hz), 7.32 (t, 1H, ^3J = 7.9 Hz), 6.94−6.87 (m, 5H), 3.86 (s, 3H), 3.84 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 162.1, 159.6, 145.5, 143.5, 132.7, 129.3, 123.1, 121.3, 116.5, 114.3, 113.1, 113.1, 55.9, 55.6, 52.1; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 272. Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92. Found: C, 70.17; H, 6.08.

9-(3′,5-Dimethoxy-[1,1′-biphenyl]-2-yl)-3,6-dimethoxy-9*H*-fluoren-9-ol (26). A solution of 2,2′-dibromo-5,5′-dimethoxy-[1,1′-biphenyl] (**25**; 2.42 g, 6.50 mmol)[48] in diethyl ether (50 mL) was stirred under N_2 at −10 °C and treated dropwise with butyllithium (5.2 mL, 2.5 M in hexane, 13 mmol). The mixture was kept at −10 °C for 30 min, and a solution of methyl 5,3′-dimethoxybiphenyl-2-carboxylate (**24**; 1.77 g, 6.50 mmol) in diethyl ether (25 mL) was added dropwise. The resulting mixture was stirred at −10 °C for 30 min and at 25 °C for 2 h. Water was added, and the phases were separated. The organic layer was washed with water and brine, dried over Na_2SO_4, and filtered. Volatiles were removed under reduced pressure, and the residue was purified by flash chromatography (silica, CH_2Cl_2 (98%)/acetone (2%)) to afford 9-(3′,5-dimethoxy-[1,1′-biphenyl]-2-yl)-3,6-dimethoxy-9*H*-fluoren-9-ol (**26**; 1.48 g, 3.26 mmol, 50%) as a colorless solid. The product was unstable and was used directly without any further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, 1H, ^3J = 8.8 Hz), 7.09−7.01 (m, 3H), 6.68 (t, 2H, ^3J = 8.3 Hz), 6.65−6.55 (m, 3H), 6.47 (d, 1H, ^4J = 2.8 Hz), 6.43−6.40 (m, 1H), 5.63 (d, 1H, ^3J = 7.5 Hz), 5.57 (m, 1H), 3.79 (s, 6H), 3.78 (s, 3H), 3.41 (s, 3H); MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 454.

3,3′,6,6′-Tetramethoxy-9,9′-spirobi[9*H*-fluorene] (27). A solution of 9-(3′,5-dimethoxy-[1,1′-biphenyl]-2-yl)-3,6-dimethoxy-9*H*-fluoren-9-ol (**26**; 702 mg, 1.54 mmol) in a mixture of concentrated aqueous HCl (1 mL) and acetic acid (10 mL) was heated at reflux for 2 h. The mixture was then cooled, diluted with water, and extracted with $CH_3COOC_2H_5$ (2 × 25 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (3 × 25 mL), water (25 mL), and brine (25 mL). After the organic phase was dried over Na_2SO_4 and filtered, volatiles were removed under reduced pressure. The residue was dissolved in the minimum amount of CH_2Cl_2 and filtered through a plug of silica gel, using CH_2Cl_2 as the eluent. The filtrate was concentrated under reduced pressure, and the residue was crystallized from $CHCl_3$/hexane to afford 3,3′,6,6′-tetramethoxy-9,9′-spirobi[9*H*-fluorene] (**27**; 553 mg, 1.27 mmol, 82%) as a colorless solid: mp 197−198 °C; IR (KBr) 1610, 1581, 1492, 1460, 1430, 1305, 1286, 1276, 1244, 1227, 1200, 1175, 1160, 1031 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, 4H, ^4J = 2.2 Hz), 6.69 (dd, 4H, ^3J = 8.3 Hz, ^4J = 2.2 Hz), 6.66 (d, 4H, ^3J = 8.3 Hz), 3.90 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 142.6, 141.9, 124.4, 113.8, 105.0, 63.4, 55.4; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 436. Anal. Calcd for $C_{29}H_{24}O_4$: C, 79.80; H, 5.54. Found: C, 79.57; H, 5.53.

3,3′,6,6′-Tetrahydroxy-9,9′-spirobi[9*H*-fluorene] (28). A solution of 3,3′,6,6′-tetramethoxy-9,9′-spirobi[9*H*-fluorene] (**27**; 538 mg, 1.23 mmol) in anhydrous CH_2Cl_2 (10 mL) was stirred under N_2 at 0 °C and treated dropwise with BBr_3 (15 mL, 1.0 M in CH_2Cl_2, 15 mmol). The mixture was stirred at 0 °C for 30 min and at 25 °C for 24 h. Water was then added, and the organic layer was extracted with 1 N aqueous NaOH (4 × 15 mL). The combined aqueous extracts were acidified with concentrated aqueous HCl and extracted with $CH_3COOC_2H_5$. The organic phase was dried over $MgSO_4$ and filtered, and volatiles were then removed under reduced pressure. The residue was dissolved in the minimum amount of $CH_3COOC_2H_5$, and the solution was filtered through a plug of silica gel using $CH_3COOC_2H_5$ as the eluent. The filtrate was concentrated under reduced pressure, and the residue was crystallized from $CH_3COOC_2H_5$/hexane to afford 3,3′,6,6′-tetrahydroxy-9,9′-spirobi[9*H*-fluorene] (**28**; 425 mg, 1.12 mmol, 91%) as a colorless solid: mp 196−198 °C; IR (KBr) 3420, 1611, 1587, 1452, 1384, 1303, 1236, 1163 cm^{-1}; H NMR (400 MHz, acetone-d_6) δ 8.28 (bs, 4H), 7.27 (d, 4H, ^4J = 2.2 Hz), 6.60 (dd, 4H, ^3J = 8.1 Hz, ^4J = 2.2 Hz), 6.46 (d, 4H, ^3J = 8.1 Hz); ^{13}C NMR (100 MHz, acetone-d_6) δ 157.7, 143.3, 141.6, 124.6, 115.3, 106.9, 60.0; MS (EI+) 380.1; HRMS (EI+) calcd for $C_{25}H_{16}O_4$ *m*/*e* 380.104859, found 380.104254.

Tetrakis(trifluoromethanesulfonate) (29) of 3,3′,6,6′-Tetrahydroxy-9,9′-spirobi[9*H*-fluorene] (28). A solution of 3,3′,6,6′-tetrahydroxy-9,9′-spirobi[9*H*-fluorene] (**28**; 423 mg, 1.11 mmol) in pyridine (10 mL) was stirred at −20 °C under N_2 and treated dropwise with $(CF_3SO_2)_2O$ (1.2 mL, 7.1 mmol).

The mixture was stirred at −20 °C for 1 h and at 25 °C for 24 h. The mixture was then diluted with water and extracted with diethyl ether. The organic layer was washed with water and brine, dried over $MgSO_4$, and filtered. Volatiles were then removed under reduced pressure, and the residue was dissolved in the minimum amount of CH_2Cl_2 and filtered through a plug of silica gel using CH_2Cl_2 as the eluent. The filtrate was concentrated under reduced pressure to afford the tetrakis(trifluoromethanesulfonate) of 3,3′,6,6′-tetrahydroxy-9,9′-spirobi[9*H*-fluorene] (**29**; 706 mg; 0.777 mmol, 70%) as a colorless solid that was used without any further purification: mp 171−172 °C; IR (KBr) 1433, 1248, 1216, 1139, 893 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, 4H, ^4J = 2.2 Hz), 7.14 (dd, 4H, ^3J = 8.4 Hz, ^4J = 2.2 Hz), 6.84 (d, 4H, ^3J = 8.4 Hz); ^{13}C NMR (100.1 MHz, $CDCl_3$) δ 150.4, 147.3, 142.6, 126.3, 122.6, 119.1 (q, J_{C-F} = 320 Hz), 114.7, 64.7; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −75.5; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 907; HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{29}H_{12}F_{12}O_{12}S_4$ *m*/*e* 907.90198, found 907.90400.

3,3′,6,6′-Tetracyano-9,9′-spirobi[9*H*-fluorene] (30). A solution of $Pd_2(dba)_3$ (27 mg, 0.029 mmol)[58] and 1,1′-bis(diphenylphosphino)ferrocene (58.1 mg, 0.105 mmol) in dry DMF (3 mL) was stirred at 25 °C under N_2, the tetrakis(trifluoromethanesulfonate) of 3,3′,6,6′-tetrahydroxy-9,9′-spirobi[9*H*-fluorene] (**29**; 300 mg, 0.330 mmol) was added, and the resulting mixture was heated at 80 °C. $Zn(CN)_2$ (102 mg, 0.869 mmol) was then added in 20 portions over a 3 h period, and the mixture was stirred at 80 °C for 24 h. The resulting suspension was cooled, filtered, and partitioned between CH_2Cl_2 and water. The organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was then dissolved in a 7:3 mixture of $CH_3COOC_2H_5$ and hexane (5 mL) and filtered through a plug of silica gel using the same mixture of solvents as eluent (100 mL). The filtrate was then concentrated under reduced pressure, and the residue was purified by flash chromatography (silica, CH_2Cl_2 (99%)/acetone (1%)) to afford 3,3′,6,6′-tetracyano-9,9′-spirobi[9*H*-fluorene] (**30**; 90 mg, 0.22 mmol, 67%) as a colorless solid: mp >300 °C; IR (KBr) 2228, 1610, 1486, 1401, 824 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 8.65 (s, 4H), 7.71 (dd, 4H, ^3J = 7.9 Hz, ^4J = 1.3 Hz), 7.08 (d, 4H, ^3J = 7.9 Hz); ^{13}C NMR (75.5 MHz, acetone-d_6) δ 151.9, 142.3, 134.0, 126.4, 126.2, 119.0, 113.9, 67.4; MS (EI+) 416; HRMS (EI+) calcd for $C_{29}H_{12}N_4$ *m*/*e* 416.106197, found 416.106329.

Tecton 19. A mixture of 3,3′,6,6′-tetracyano-9,9′-spirobi[9*H*-fluorene] (**30**; 305 mg, 0.732 mmol), dicyandiamide (985 mg, 11.7 mmol), and powdered KOH (104 mg, 1.85 mmol) in 2-methoxyethanol (10 mL) was heated at reflux for 24 h. The mixture was then cooled, and water (20 mL) was added. The resulting solid was filtered, washed thoroughly with hot water, and then dried in vacuo to give tecton **19** (398 mg, 0.529 mmol, 72%) as a colorless solid: mp >300 °C; IR (KBr) 3400, 1607, 1541, 1457, 1433, 1381, 815 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.83 (s, 4H), 8.10 (d, 4H, ^3J = 8.0 Hz), 6.83 (d, 4H, ^3J = 8.0 Hz), 6.98−6.67 (bs, 16H); ^{13}C NMR (100.1 MHz, CF_3COOD) δ 165.4, 161.6, 156.0, 143.6, 131.7, 130.8, 127.2, 123.0, 68.6. MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 753.8 (M + 1); HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{37}H_{29}N_{20}$ *m*/*e* 753.288406, found 753.287000.

2,2′,7,7′-Tetranitro-9,9′-spirobi[9*H*-fluorene] (31). Fuming nitric acid (40 mL) was stirred at 0 °C, and 9,9′-spirobi[9*H*-fluorene] (**17**; 7.18 g, 22.7 mmol)[44] was added in small portions during 20 min. The resulting mixture was kept at 0 °C for 1 h, and a mixture of acetic anhydride (15 mL) and acetic acid (25 mL) was slowly added. The resulting precipitate was filtered, washed abundantly with acetic acid and water, and dried in vacuo to afford 2,2′,7,7′-tetranitro-9,9′-spirobi[9*H*-fluorene] (**31**; 8.42 g, 17.0 mmol, 75%) as a light yellow solid. A sample of analytical purity was obtained by crystallization from THF/hexane: mp >300 °C; IR (KBr) 1589, 1522, 1340, 1077 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.58 (d, 4H, ^3J = 8.5 Hz), 8.45 (dd, 4H, ^3J = 8.5 Hz, ^4J = 2.0 Hz), 7.63 (d, 4H, ^4J = 2.0 Hz); ^{13}C NMR (100.1 MHz, DMSO-d_6) δ 149.3, 148.5, 146.7, 126.2, 124.8, 120.0, 65.9; HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{25}H_{13}N_4O_8$ *m*/*e* 497.073339, found 497.075500. Anal. Calcd for $C_{25}H_{12}N_4O_8$: C, 60.49; H, 2.44. Found: C, 60.59; H, 2.43.

2,2′,7,7′-Tetraamino-9,9′-spirobi[9*H*-fluorene] (32). A suspension of 2,2′,7,7′-tetranitro-9,9′-spirobi[9*H*-fluorene] (**31**; 8.30 g, 16.7 mmol) and 10% Pd/C (800 mg) in THF (250 mL) was stirred for 24 h in a Parr reactor at 25 °C under H_2 (160 psi). The resulting mixture was filtered through Celite using THF as eluent, and the filtrate was concentrated under reduced pressure. This yielded a residue of 2,2′,7,7′-tetraamino-9,9′-spirobi[9*H*-fluorene] (**32**; 6.16 g, 16.4 mmol, 98%) as a colorless solid, which was used without further purification: mp >210 °C (dec); IR (KBr) 3427, 3383, 3344, 1699, 1620, 1579, 1439, 1313, 1232, 1120, 880 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.38 (d, 4H, ^3J = 8.0 Hz), 6.59 (dd, 4H, ^3J = 8.0 Hz, ^4J = 2.0 Hz), 5.93 (d, 4H, ^4J = 2.0 Hz), 4.35 (bs, 8H); ^{13}C NMR (100.1 MHz, DMSO-d_6) δ 151.3, 147.9, 131.7, 119.5, 113.8, 110.4, 65.7; MS (EI+) *m*/*e* 376; HRMS (EI+) calcd for $C_{25}H_{20}N_4$ *m*/*e* 376.168797, found 376.168412.

2,2′,7,7′-Tetra(acetamido)-9,9′-spirobi[9*H*-fluorene] (33). A solution of 2,2′,7,7′-tetraamino-9,9′-spirobi[9*H*-fluorene] (**32**; 6.38 g, 16.9 mmol) in acetic acid (200 mL) was stirred vigorously at 0 °C and treated dropwise with acetic anhydride (200 mL) over a 30 min period. The resulting suspension was stirred at 25 °C for 18 h and then diluted with CH_2Cl_2 (500 mL). The resulting precipitate was filtered and dissolved in DMF (150 mL), and the solution was poured into cold water with vigorous stirring. The resulting precipitate was separated by filtration, washed with water, and dried to afford a pure sample of 2,2′,7,7′-tetra(acetamido)-9,9′-spirobi[9*H*-fluorene] (**33**; 8.98 g, 16.5 mmol, 98%) as an off-white solid: mp >300 °C; IR (KBr) 3300, 1668, 1596, 1548, 1469, 1412, 1370, 1312, 1255, 815 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 9.80 (s, 4H), 7.80 (d, 4H, ^3J = 8.3 Hz), 7.59 (dd, 4H, ^3J = 8.3 Hz, ^4J = 1.8 Hz), 6.86 (d, 4H, ^4J = 1.8 Hz), 1.89 (s, 12H); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 168.9, 149.9, 139.6, 136.8, 121.0, 119.5, 114.7, 66.3, 24.8; HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{33}H_{29}N_4O_4$ *m*/*e* 545.218881, found 545.220400.

2,2′,7,7′-Tetra(acetamido)-3,3′,6,6′-tetranitro-9,9′-spirobi[9*H*-fluorene] (34). 2,2′,7,7′-Tetra(acetamido)-9,9′-spirobi[9*H*-fluorene] (**33**; 2.18 g, 4.00 mmol) was added in small portions over a 10 min period to fuming nitric acid (20 mL) stirred at −10 °C. The mixture was kept at this temperature for 20 min and was then poured into cold water (400 mL). The resulting precipitate was filtered, washed with water, and dried. The solid was crystallized from THF/hexane to afford 2,2′,7,7′-tetra(acetamido)-3,3′,6,6′-tetranitro-9,9′-spirobi[9*H*-fluorene] (**34**; 2.80 g, 3.86 mmol, 97%) as a yellow solid: mp >300 °C; IR (KBr) 3400, 1702, 1623, 1585, 1483, 1418, 1384, 1330, 1290, 1232 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.19 (s, 4H), 8.88 (s, 4H), 6.96 (s, 4H), 1.90 (s, 12H); ^{13}C NMR (100.1 MHz, DMSO-d_6) δ 167.9, 150.2, 143.5, 135.9, 131.1, 119.8, 118.2, 64.3, 22.6; MS (FAB, 3-nitrobenzyl alcohol) *m*/*e* 725 (M + 1); HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{33}H_{24}N_8O_{12}$ *m*/*e* 725.159194, found 725.161500.

2,2′,7,7′-Tetraamino-3,3′,6,6′-tetranitro-9,9′-spirobi[9*H*-fluorene] (35). A suspension of 2,2′,7,7′-tetra(acetamido)-3,3′,6,6′-tetranitro-9,9′-spirobi[9*H*-fluorene] (**34**; 1.78 g, 2.46 mmol) in aqueous 3 N KOH (50 mL) was stirred at 50 °C for 24 h. The suspension was cooled, and the resulting precipitate was filtered, washed with water, and dried in vacuo. The solid was crystallized from THF/hexane to afford 2,2′,7,7′-tetraamino-3,3′,6,6′-tetranitro-9,9′-spirobi[9*H*-fluorene] (**35**; 1.31 g, 2.35 mmol, 96%) as a red solid: mp >250 °C (dec); IR (KBr) 3478, 3367, 1637, 1591, 1495, 1463, 1431, 1392, 1333, 1308, 1271, 1225, 1187 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.70

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[58] Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

(s, 4H), 7.40 (s, 8H), 6.45 (s, 4H); ^{13}C NMR (100.1 MHz, DMSO-d_6) δ 156.4, 147.2, 131.8, 128.5, 118.0, 114.6, 64.3; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 556; HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{25}H_{17}N_8O_8$ *m/e* 557.116935, found 557.118800. Anal. Calcd for $C_{25}H_{16}N_8O_8 \cdot 0.5$ THF$\cdot H_2O$: C, 53.12; H, 3.63; N, 18.35. Found: C, 53.04; H, 3.37; N, 18.39.

3,3′,6,6′-Tetranitro-9,9′-spirobi[9*H*-fluorene] (36). A mixture of isoamyl nitrite (40 mL) in anhydrous DMF (75 mL) was stirred at 65 °C under N_2 and treated dropwise with a solution of 2,2′,7,7′-tetraamino-3,3′,6,6′-tetranitro-9,9′-spirobi[9*H*-fluorene] (**35**; 3.01 g, 5.41 mmol) in DMF (75 mL). The mixture was stirred at 65 °C for 3 h, cooled to room temperature, and partitioned between $CH_3COOC_2H_5$ and water. The organic phase was washed several times with water, aqueous 1 N HCl, and brine. It was then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was dissolved in the minimum amount of CH_2Cl_2 and filtered through a plug of silica gel using CH_2Cl_2 as eluent. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica, CH_2Cl_2 (80%)/hexane (20%)) to afford 3,3′,6,6′-tetranitro-9,9′-spirobi[9*H*-fluorene] (**36**; 0.834 g, 1.68 mmol, 31%) as a light yellow solid: mp >300 °C; IR (KBr) 1516, 1343 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 (d, 4H, $^4J = 2.0$ Hz), 8.17 (dd, 4H, $^3J = 8.4$ Hz, $^4J = 2.0$ Hz), 6.92 (d, 4H, $^3J = 8.4$ Hz); ^{13}C NMR (100.1 MHz, DMSO-d_6) δ 153.3, 149.8, 142.4, 126.0, 125.6, 118.9, 65.7; MS (EI+) *m/e* 496; HRMS (EI+) calcd for $C_{25}H_{12}N_4O_8$ *m/e* 496.065514, found 496.065354.

3,3′,6,6′-Tetraamino-9,9′-spirobi[9*H*-fluorene] (37). A procedure analogous to the one used to reduce tetranitrospirobifluorene **31** was carried out using 3,3′,6,6′-tetranitro-9,9′-spirobi[9*H*-fluorene] (**36**; 805 mg, 1.62 mmol) in contact with 10% Pd/C (380 mg) and H_2 during 72 h. The reaction provided 3,3′,6,6′-tetraamino-9,9′-spirobi[9*H*-fluorene] (**37**; 565 mg, 1.50 mmol, 93%) as a light yellow solid: mp >300 °C; IR (KBr) 3409, 2924, 2859, 1612, 1497, 1460, 1309, 1255, 1177, 1053 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.85 (d, 4H, $^4J = 1.9$ Hz), 6.26 (dd, 4H, $^3J = 8.0$ Hz, $^4J = 1.9$ Hz), 6.18 (d, 4H, $^3J = 8.0$ Hz), 5.00 (bs, 8H); ^{13}C NMR (100.1 MHz, DMSO-d_6) δ 148.8, 142.9, 139.1, 124.3, 114.4, 105.5, 63.7; HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{25}H_{21}N_4$ *m/e* 377.176622, found 377.175900.

Tecton 20. A solution of cyanuric chloride (738 mg, 4.00 mmol) in acetone (10 mL) was stirred at −10 °C and treated dropwise with a solution of 3,3′,6,6′-tetraamino-9,9′-spirobi[9*H*-fluorene] (**37**; 347 mg, 0.922 mmol) in acetone (10 mL). The mixture was stirred at −10 °C for 1 h, and Na_2CO_3 (424 mg, 4.00 mmol) was added. The resulting suspension was poured into cold water (100 mL), and the precipitate was filtered, washed thoroughly with cold water, and dried. The solid was then dissolved in dioxane (10 mL), and the mixture was treated with concentrated aqueous NH_4OH (10 mL) and heated at reflux for 18 h. The resulting suspension was cooled, and water (25 mL) was added. The precipitate was filtered, washed thoroughly with water, and dried to afford tecton **20** (468 mg, 0.576 mmol, 62%) as an off-white solid: mp >300 °C; IR (KBr) 3400, 1607, 1552, 1438, 1407, 812 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) 8.85 (m, 4H), 8.11 (m, 4H), 7.44 (m, 4H), 6.44 (m, 4H), 6.30 (bs, 16H); ^{13}C NMR (100.1 MHz, DMSO-d_6, 25 °C) δ 168.2, 165.9, 143.4, 142.4, 141.0, 123.9, 121.5, 113.2, 66.0; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 813 (M + 1); HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{37}H_{33}N_{24}$ *m/e* 813.332003, found 813.334300.

2,2′,7,7′-Tetracyano-9,9′-spirobi[9*H*-fluorene] (42). A mixture of 2,2′,7,7′-tetrabromo-9,9′-spirobi[9*H*-fluorene] (**41**; 1.26 g, 1.99 mmol)[44] and CuCN (0.806 g, 9.00 mmol) in DMF (10 mL) was heated at reflux for 24 h under N_2. The resulting mixture was cooled, diluted with water (100 mL) and ethylenediamine (10 mL), and extracted with CH_2Cl_2 (3 × 75 mL). The combined organic extracts were washed with 10% aqueous NaCN, water, and brine. The organic phase was then dried over $MgSO_4$ and filtered. Volatiles were removed under reduced pressure, and the residue was purified by flash chromatography (silica, CH_2Cl_2) to afford 2,2′,7,7′-tetracyano-9,9′-spirobi[9*H*-fluorene] (**42**; 0.662 g, 1.60 mmol, 80%) as a colorless solid: mp >300 °C; IR (KBr) 2231, 1604, 1573, 1501, 1448, 1406, 1073, 910, 833 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, 4H, $^3J = 8.0$ Hz), 7.84 (dd, 4H, $^3J = 8.0$ Hz, $^4J = 1.3$ Hz), 7.02 (d, 4H, $^4J = 1.3$ Hz); ^{13}C NMR (100.1 MHz, $CDCl_3$) δ 147.5, 144.3, 134.0, 128.2, 122.9, 118.3, 113.9, 65.5; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 417 (M + 1); HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{29}H_{13}N_4$ *m/e* 417.114022, found 417.113100.

Tecton 39. A procedure analogous to the one used to synthesize tecton **19** was carried out using 2,2′,7,7′-tetracyano-9,9′-spirobi[9*H*-fluorene] (**42**; 227 mg, 0.545 mmol). This provided tecton **39** (343 mg, 0.456 mmol, 84%) as a colorless solid: mp >300 °C; IR (KBr) 3469, 3387, 1609, 1537, 1418, 1382, 814 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.42 (d, 4H, $^3J = 8.1$ Hz), 8.25 (d, 4H, $^3J = 8.1$ Hz), 7.57 (s, 4H), 6.68 (bs, 16H); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 168.7, 166.7, 148.0, 143.0, 137.2, 127.9, 122.2, 120.6, 64.8; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 753 (M + 1); HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $C_{37}H_{29}N_{20}$ *m/e* 753.28839, found 753.29010.

Tecton 40. A procedure analogous to the one used to synthesize tecton **20** was carried out using 2,2′,7,7′-tetraamino-9,9′-spirobi[9*H*-fluorene] (**32**; 376 mg, 0.999 mmol). This provided tecton **40** (585 mg, 0.720 mmol, 72%) as a colorless solid: mp >300 °C; IR (KBr) 3390, 1618, 1547, 1467, 1448, 1419, 1384 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.58 (s, 4H), 8.23 (d, 4H, $^3J = 8.4$ Hz), 7.73 (d, 4H, $^3J = 8.4$ Hz), 6.55 (s, 4H), 6.19 (bs, 16H); ^{13}C NMR (100.1 MHz, DMSO-d_6) δ 167.9, 165.5, 149.8, 140.4, 135.7, 120.7, 120.0, 115.7, 66.2; MS (FAB, 3-nitrobenzyl alcohol) *m/e* 813 (M + 1). Anal. Calcd for $C_{37}H_{32}N_{24} \cdot$dioxane$\cdot H_2O$: C, 53.59; H, 4.61. Found: C, 53.39; H, 4.32.

X-ray Crystallographic Studies. The structures were solved by direct methods using SHELXS-97 and refined with SHELXL-97.[59] All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed in ideal positions and refined as riding atoms.

Structure of 3,3′,6,6′-Tetrahydroxy-9,9′-spirobi[9*H*-fluorene] (28). Crystals of the compound **28** belong to the triclinic space group *P*-1 with $a = 7.5560(3)$ Å, $b = 11.3326(4)$ Å, $c = 17.5119(7)$ Å, $\alpha = 85.896(2)°$, $\beta = 77.828(3)°$, $\gamma = 73.671(2)°$, $V = 1406.57(9)$ Å^3, $D_{calcd} = 1.314$ g cm^{-3}, and $Z = 2$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0597$ and $R_w = 0.1649$ for 3767 reflections with $I > 2\sigma(I)$.

Structure of 2,2′,7,7′-Tetra(acetamido)-9,9′-spirobi[9*H*-fluorene] (33). Crystals of compound **33** belong to the monoclinic space group *C*2/*c* with $a = 20.504(8)$ Å, $b = 12.2870(7)$ Å, $c = 16.8890(4)$ Å, $\beta = 120.36(5)°$, $V = 3671.4(14)$ Å^3, $D_{calcd} = 1.195$ g cm^{-3}, and $Z = 4$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0663$ and $R_w = 0.2090$ for 3418 reflections with $I > 2\sigma(I)$.

Structure of Tecton 39. Crystals of compound **39** belong to the orthorhombic space group *Pcca* with $a = 21.506(8)$ Å, $b = 15.279(5)$ Å, $c = 21.305(7)$ Å, $V = 7001(4)$ Å^3, $D_{calcd} = 1.425$ g cm^{-3}, and $Z = 4$. Only part of the included molecules could be resolved. The SQUEEZE option of the program PLATON[19] was used to eliminate the contribution of included molecules (dioxane) that were highly disordered, thereby giving final models based only on the ordered part of the structure. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0913$ and $R_w = 0.2847$ for 5042 reflections with $I > 2\sigma(I)$.

Structure of Tecton 40. Crystals of compound **40** belong to the tetragonal space group *P*-4*b*2 with $a = b = 23.519(4)$ Å, $c = 10.2647(13)$ Å, $V = 5677.8(14)$ Å^3, $D_{calcd} = 1.253$ g cm^{-3},

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(59) Sheldrick, G. M. *SHELXS-97, Program for the Solution of Crystal Structures* and *SHELXL-97, Program for the Refinement of Crystal Structures*; Universität Göttingen: Germany, 1997.

and $Z = 2$. Only part of the included molecules could be resolved. The SQUEEZE option of the program PLATON[19] was used to eliminate the contribution of included molecules that were highly disordered, thereby giving final models based only on the ordered part of the structure. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0743$ and $R_w = 0.1838$ for 4057 reflections with $I > 2\sigma(I)$.

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Supporting Information Available: General experimental procedures; crystallization of compounds **28**, **33**, **39**, and **40**; ORTEP drawings and tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compounds **28**, **33**, **39**, and **40**; comparison of the porosities of selected molecular crystals; and ^{1}H and ^{13}C NMR spectra for compounds **19**−**20**, **26**, **28**−**30**, **32**−**34**, **36**−**37**, **39**, and **42**. This information is available free of charge via the Internet at http://pubs.acs.org.

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