Nanoassembly of a Fractal Polymer: A Molecular Sierpinski "Hexagonal Gasket"

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Mathematics and art converge in the fractal forms that also abound in nature. Here we use molecular self-assembly to create a synthetic, nanometer-scale Sierpinski hexagonal gasket. This non-dendritic, perfectly self-similar fractal macromolecule is comprised of *bis*terpyridine building blocks that are bound together by coordination to 36 Ru and 6 Fe ions to form a nearly planar array of increasingly larger hexagons around a hollow center.

Fractal constructs are based on the incorporation of identical motifs that repeat on differing size scales (*1*). Examples of fractal shapes in nature include clouds, trees, waves on a lake, the human circulatory system, and mountains, to mention but a few. The study of fractals has moved from the field of pure mathematics, to descriptions of nature that, in turn, inspired artistic design. More recently, chemists have incorporated the fractal form in molecular synthesis. Since 1985, molecular trees, which generally branch in a binary (*2*) or ternary (*3*) pattern, have been synthesized with increasing size and structural complexity. Beyond their aesthetics, these dendrimers and hyperbranched materials (*4*) are now under study for a wide range of practical applications. However, tree-like patterns are but one type of fractal comprised of repeating geometrical figures. A porphyrin-based dendrimer (*5*) that uses porphyrins as branching centers has been prepared that incorporates the snake-like "Kolam" fractal pattern described by Ascher (*6*). Nonetheless, most mathematically-defined fractals have yet to be produced in the laboratory.

The first mathematically-defined fractal was derived in 1915 (*7*), when the Polish mathematician Vacłav Sierpinski described a series of interrelated equilateral triangles, later coined by Mandelbrot as the "Sierpinski Gasket".(*1*) The original equation has been expanded into other fractal constructs called Sierpinski "n-gons" including the beautiful hexagonal gasket. Mathematically, such fractal hexagonal structures result by operating on the points in a hexagon H_0 with six functions

$$f_j(x, y) = \begin{bmatrix} 1/3 & 0 \\ 0 & 1/3 \end{bmatrix} \left(\begin{bmatrix} x \\ y \end{bmatrix} \right) + P_j, \ J = 1,..., 6$$

where P_j are the vertices of H_0. Iteratively, this relation leads to: $H_{j+1} = f_1(H_j) + f_2(H_j) + f_3(H_j) + f_4(H_j) + f_5(H_j) + f_6(H_j)$, and the sequence $\{H_j\}$ converges to the hexagonal gasket shown in Fig 1. This mathematically-defined fractal pattern – the "Sierpinski hexagonal gasket" – offered a significant synthetic challenge for chemical self-assembly (*8-11*) given the size and complexity of the target.

Herein, we report the chemical synthesis of a non-dendritic fractal construct, based on Sierpinski's hexagonal gasket (incorporating both the Star of David and a Koch snowflake) where the terminology 'non-dendritic' refers to repeat units that do not branch in the typical tree-like pattern. To create the desired repeat unit, we built on our recent studies of metallohexamer formation (*12-14*), in which the facile self-assembly of a *meta*(*bis*-terpyridinyl)benzene (*12, 13, 15*), in the presence of one equivalent of a metal ion, e. g., Fe(II), affords a high yield of the desired hexagonal product (*14*).

Initially, 1 equiv. of *bis*-[Ru(III)] monomer **1** was heated with 4.5 equiv. of *tris*terpyridine(*16*) **2** in refluxing CHCl₃/CH₃OH for 20 h under reducing conditions (added *N*-ethylmorpholine) to give the pivotal hetero-trimer **3**, as deep red microcrystals in 35% yield (Fig. 2). Its ¹H nuclear magnetic resonance (NMR) spectrum exhibited two singlets at 9.32 and 9.28 ppm in a 1:1 ratio, attributed to the four inner and outer 3',5'-tpy*H*s (where tpy = terpyridine) of the complexed ligands, as well as a resonance at 9.08 ppm assigned to the eight remaining 3',5'-tpy*H*s of the uncomplexed terpyridines, which integrated in a 2:1 ratio to

the former downfield peaks; also, a singlet was observed at 2.89 ppm for the methyl groups. Electrospray ionization mass spectroscopy (ESI-MS) [$C_{139}H_{92}F_{24}N_{24}P_{12}Ru_2$ (2880.38): observed peaks at m/z: 2736.6 $(M - PF_6)^+$, 1295.9 $(M - 2PF_6)^{2+}$] gave further evidence for the desired structure. Following purification of building blocks **3**, **4**, and **5** using a mixture of $H_2O:KNO_3:CH_3CN$, the counter ions were converted to PF_6^- to facilitate a homogeneous ionic environment for ESI-MS analysis.

Treatment of **3** with homotrimer **4** in the presence of *N*-ethylmorpholine produced the desired red microcrystalline hexamer **5** in 31% yield; this structure was also confirmed by the ratio of the proton resonances (NMR) for the complexed and uncomplexed 3',5'-tpy*H*s. The ESI-MS (expected mass for the $C_{250}H_{170}F_{72}N_{42}P_{12}Ru_6$ cationic core and counter ions = 6108.30) definitively showed the multiple-charged signals ranging from m/z at 1077.8 $(M - 5\ PF_6)^{5+}$ to 364.2 $(M - 12\ PF_6)^{12+}$ for the expected charge states. Treatment of hexamer **5** with one equivalent of $FeCl_2$ in refluxing CH_3OH resulted in the one-step self-assembly of the desired fractal gasket **6**, isolated in 35% yield, as a deep red solid. Column chromatography and dialysis removed the low molecular weight monomers as well as the linear, oligomeric materials. This material isolated as the polyCl^- salt showed good solubility in CH_3OH, EtOH, DMF, and DMSO and poor solubility in H_2O, CH_2Cl_2, CH_3CN; whereas, following counter ion exchange to the polyPF_6^- salt changes that trend to make them soluble in CH_3CN, DMF, and DMSO and insoluble in CH_3OH, EtOH, and CH_2Cl_2.

The characterization of gasket **6** involved a considerable range of spectroscopic and electron microscopy techniques. Taken together, the data offered strong support for the proposed structure.

The use of a different metal in the last assembly step was planned, because different spectral properties using Fe(II) vs. Ru(II) connectivity would aid in the molecular characterization; notably, the all Ru(II) counterpart was easily formed by the use of $[Ru(DMSO)_4Cl_2]$ in the final macrocyclization. In the case of the Fe-Ru construct, there should be a 1:6 Fe:Ru ratio observed for all macromolecules generated. Formation of the heterodinuclear construct was initially confirmed by ^{1}H NMR measurements that showed two characteristic 3',5'-tpy*H* peaks one at 9.45 ppm attributed to the tpy-*Fe*-tpy complex and the other at 9.20 ppm attributed to the tpy-*Ru*-tpy complex, displaying the requisite 1:6 integration; a distinct singlet at 2.98 ppm for the methyl groups was also present. Ultraviolet visible (UV-vis) spectroscopy in CH_3CN (for PF_6^-) or CH_3OH (for Cl^-) showed the expected absorbance pattern at 575 and 495 nm with a 1:6 ratio for the tpy-*Fe*-tpy and tpy-*Ru*-tpy units, respectively. These results are consistent with that observed in a previous study (*17*) where a hexagonal

metallomacrocycle possessing 3 Fe and 3 Ru ions was prepared in an alternating pattern. As well, the individual $(tpy)_2$Fe (*18*) and $(CH_3C_6H_4tpy)_2$Ru (*19*) complexes were shown to have absorptions at 562 and 490, respectively; thus little or no cooperative effects can be attributed to the larger structures. Due to the overall 84^+ molecular charge, matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF MS) measurements failed to provide definitive structural information; however, the ESI-MS spectrum showed a broad peak range from m/z at 310 to 970 attributed to the multi-charged stages m/z = 35^+ to 84^+. A recent investigation (*20*) concerning *bis*(tpy)Ru(II)-based macrocycles has determined the ESI technique to be superior to the MALDI technique because it has the advantages of direct detection of multiply charged ions, it does not change the complex connectivity through disassembly and reassembly processes, and it effects very little or no fragmentation.

The cyclic voltammogram (CV) of gasket **6** (see supporting online material) exhibits two reductive couples and one oxidative couple. The first and second reductive couples are not reversible and the first has a sharp oxidative peak that grows with each succesive scan due to adsorption on the electrode surface. The third redox couple observed around 1 V corresponds to the oxidation of Ru(II); however, the oxidation potential of Fe(II) is very close to this value and thus it is impossible to establish the relative currents derived from Fe vs. Ru for stoichiometric quantification. Because these metal terpyridine centers are redox independent, the electrochemical data cannot be used to confirm the structure of the fractal **6**; however, the data are entirely consistent with the proposed structure.

X-ray photoelectron spectroscopy (XPS, using monochromatic Mg Kα radiation at a power of 250 W) was undertaken in order to verify the presence of the coordinated metals and to gain more data in support of cyclic structure. This technique uses x-ray radiation to measure the characteristic electron binding energies of the elements and the intensity of the recorded peaks is related to elemental concentration. The XPS spectrum showed binding energy peaks at 398 and 285 eV attributed to the N1s and C1s electrons of the terpyridine ligands, respectively, as well as peaks assigned to Ru ($3d^{1/2}$ at 284 eV and $3d^{5/2}$ at 280 eV) and Fe ($2p^{1/2}$ at 706 eV and $2p^{3/2}$ at 709 eV) thus confirming the presence of Fe and Ru complexes. The exact atomic Ru:Fe ratio of 6:1 afforded further support for the macrocyclization of monomer **5**.

Energy minimization calculations for the desired fractal **6**, performed using molecular modeling software (see supporting online material), indicated that the predicted structure would possess a 12.3 nm diameter and 0.7 nm height; the modeled structure of fractal **6** on a mica surface

possessed a slight chair-like or bent geometry rather than strict planarity. Dynamic light scattering (DLS) experiments (see supporting information) determined the average particle size of fractal **6** to be 12.5 nm, which is the intensity-averaged hydrodynamic diameter (*21*).

Because this fractal construct possesses a uniform internal repeating (polymeric) architecture that is highly symmetrical, the NMR, UV, XPS, CV, and DLS data confirm the repeat units but do not definitively establish the overall architecture of this nanoscopic hexagonal gasket; therefore, it was necessary to undertake single molecule imaging studies. In order to visually confirm the hexagonal structure, a droplet of an acetonitrile solution of **6** (100 μg/500 ml) was deposited on the surface of freshly cleaved mica or Au(111), dried under ambient conditions, and subjected to atomic force microscopy (AFM). This technique allows the mapping of a surface with a tip on a cantilever that results in a topographic image of a surface; the size and sharpness of the tip determines the size of the objects that can be mapped with good resolution. AFM provides data on a sample's dimensions including height. The AFM images of individual fractal constructs reveal an average diameter of 20 ± 2 nm, relative to the ca. 4 nm radius of curvature of the silicone tip used in the AFM measurements (Fig. 3A) thereby supporting the modeled diameter of ca. 12 ± 2 nm (*22*). The higher magnification images exhibited clear patterns in which the six ruthenium hexamers and the central hole were clearly discernible.

Transmission electron microscopy (TEM; Fig. 3B) was also employed for characterization. TEM analysis provides the size, shape, and arrangement of a specimen and in some cases can provide crystallographic information. After casting a dilute methanol solution of **6** (250 μg/100 ml) on carbon-coated grids (Cu and Ni, 400 mesh), the resultant analysis showed the predicted fractal-like pattern (Fig. 3B) possessing an average diameter of 11 ± 1 nm for the single molecule, which gives direct evidence for the macrocyclization. Study of a higher magnification TEM image (Fig. 3B insert) reveals individual hexagonal gaskets lying flat or slightly tilted. Ultra-high vacuum low-temperature scanning tunneling microscopy (UHV-LT-STM) (*23*) was also employed to image the structure. This apparatus can generate images with atomic resolution by directly measuring electronic states. Ultra-high vacuum allows clean, controlled surface preparation and cryogenic temperatures to help reduce electronic noise and slow molecular motion. Using the same dilution employed for the TEM sample preparation, fractal construct **6** in acetonitrile was cast onto a freshly cleaned Au(111) surface. STM images acquired at 6 K (Fig. 3C) verified a hexagonal pattern of the molecule (12 ± 1 nm diameter, and ca. 0.8 nm in height), which was consistent with the computer-generated model of the structure.

Tunneling conductance spectra determined for single molecules at 6 K showed a 1 eV energy gap. Traces of linear oligomeric as well as larger macrocyclic assemblies were also observed on the STM images (see supporting information) and will be considered in detail elsewhere.

References and Notes

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Figs S1 to S7
References

Fig. 1. Sierpinski's hexagonal gasket (**A**) incorporating the Star of David and the Koch Snowflake motifs: G1-3 indicate generations 1-3 that can be envisioned for this fractal-based construct. Images of the "Snake " kolam (**B**) and the $1 \rightarrow 3$ branching pattern (**C**) of a tree.

Fig. 2. Reaction scheme for the synthesis of trimer **3**, hexamer **5**, and the fractal gasket **6**. Reaction conditions: a) **1** and **2** were mixed with N-ethylmorpholine in refluxing $CH_3OH/CHCl_3$ (2:1 v/v), for 20 h; b) **3** and **4** were stirred in refluxing CH_3OH with added N-ethylmorpholine for 12 h; c) 1. hexamer **5** was refluxed in CH_3OH in the presence of one equiv. of $FeCl_2 \cdot 6H_2O$ for 20 h, 2. To CH_3OH solution of $\mathbf{5}(Cl^-)_m(NO_3^-)_n$ was added a solution of NH_4PF_6 to obtain the desired gasket **6** as a precipitate. The representative hexagons that are noted constitute the generational growth of the fractal gasket.

Fig. 3. Images of gasket **6**: (**A**) AFM images at 1.12 x 1.12 μm and 100 x 100 nm; (**B**) TEM pictures with 50 and 20 nm scale bars for the lower and higher resolution images, respectively (all image were obtained unstained); (**C**) UHV-STM images (100 x 100 nm) on a Au(111) surface at 6 K revealing a line of gaskets settled on a ridge on the gold surface and a color enhanced and magnified image of a single molecule (scale bar = 3 nm).

A

G3

G2

G1

B

C