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Sierpiński Triangles

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One-Step Multicomponent Self-Assembly of a First-Generation Sierpiński Triangle: From Fractal Design to Chemical Reality**

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Abstract: *A novel terpyridine-based architecture that mimics a first-generation Sierpiński triangle has been synthesized by multicomponent assembly and features tpy–Cd^{II}–tpy connectivity (tpy = terpyridine). The key terpyridine ligands were synthesized by the Suzuki cross-coupling reaction. Mixing two different terpyridine-based ligands and Cd^{II} in a precise stoichiometric ratio (1:1:3) produced the desired fractal architecture in near-quantitative yield. Characterization was accomplished by NMR spectroscopy, mass spectrometry, and transmission electron microscopy.*

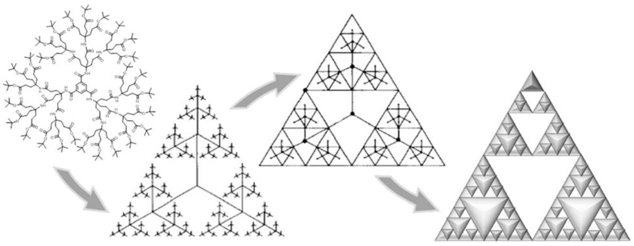

Figure 1. Conceptual progression of a 1→3 dendritic branching pattern and its geometric relationship to the classical Sierpiński triangle.[10]

Naturally occurring species often self-assemble into fractal shapes and forms.[1,2] In 1915, the Polish mathematician Waclaw Sierpiński formulated an equilateral triangular fractal, which was constructed by connecting smaller equilateral triangles[3] (Figure 1). Later, Mandlebrot described these triangular fractals as Sierpiński gaskets (triangles or sieves).[1,4] The number of triangles in a Sierpiński triangle can be found by using the formula $N_n = 3^n$, where N is the number of triangles and n the number of iterations.[5]

Simple fractal motifs have been successfully integrated into synthetic organic entities over the past forty years in the form of dendrimers.[6–9] There is a unique relationship between the 1→3 branched dendrimers[6] and the Sierpiński triangle, which is presented in Figure 1.[10,11] Recent advances in supramolecular chemistry[12] have paved the way to a better understanding of how to quantitatively assemble various simple architectures in one step,[13–22] including the desired triangular predecessor constructs.[13,14]

Coordination-driven self-assembly using tailored 2,2′:6′,2″-terpyridine (tpy) building blocks has highlighted their ability to form stable linear tpy–M^{II}–tpy complexes as the structural walls of the polygons possessing rigid organic vertices. Therefore, programmed structural features are easily incorporated into the poly(terpyridine) building blocks, generating avenues to novel nanomolecular constructs[23] in quantitative or near-quantitative yields.[24] Both homoleptic and heteroleptic connectivity has been used extensively in these assemblies, but heteroleptic assembly with a need for multicomponent building blocks still remains challenging owing to a tendency to produce competitive products.[25–27] Recently, we have reported various heteroleptic materials, such as a hexagonal spoked wheel,[28] molecular bowties and butterflies,[29] and a molecular rhombus,[30] which were obtained by either multicomponent or one-step assembly. Herein, we report the design and synthesis of a first-generation molecular Sierpiński triangle using two unique ligands with tpy–Cd^{II}–tpy connectivity (Figure 2).

Retrosynthetic analysis of the first-generation Sierpiński triangle (Figure 1) revealed that it would require two easily accessible components for its assembly: a tetrakis(terpyridine) “K” unit for the walls and the core region and a ditopic 60°-directed “V” unit for the vertices. Cadmium was chosen owing to a unique combination of thermodynamic stability and kinetic lability for its complexes. A 1:1 ratio of these “K” and “V” ligands was coupled with precisely three equivalents of Cd^{II}; the overall stability of the highly symmetric polytriangular architecture was projected to be favored over any oligomeric possibilities. In essence, there would be no loose ends or uncoordinated ligands.

Initially, a THF solution of 2,3,5,6-tetrabromocatechol and iodomethane (Scheme 1) was heated at reflux in an inert atmosphere (N_2, K_2CO_3, 12 h) to generate **3**. Boronic acid **1**[31] was prepared using commercially available 4-formylphenylboronic acid. The desired “K” ligand **4** was easily synthesized (72%) from **3** by treatment with **1** using standard Suzuki cross-coupling reaction conditions (K_2CO_3, [Pd(PPh$_3$)$_2$Cl$_2$])

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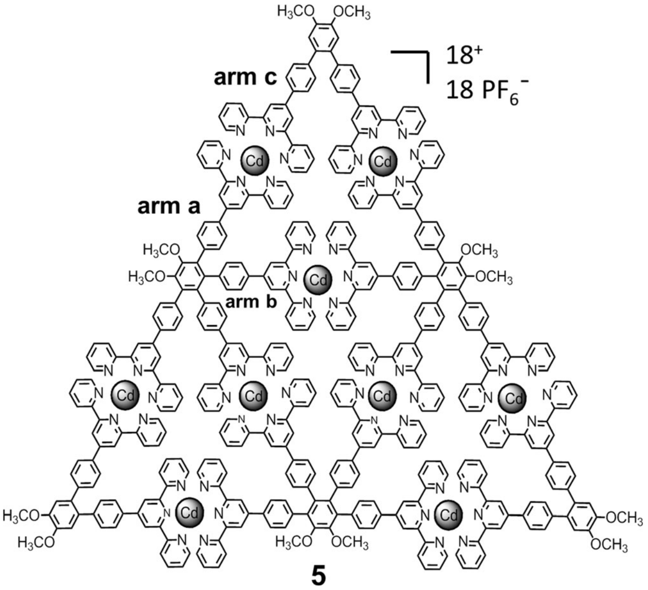
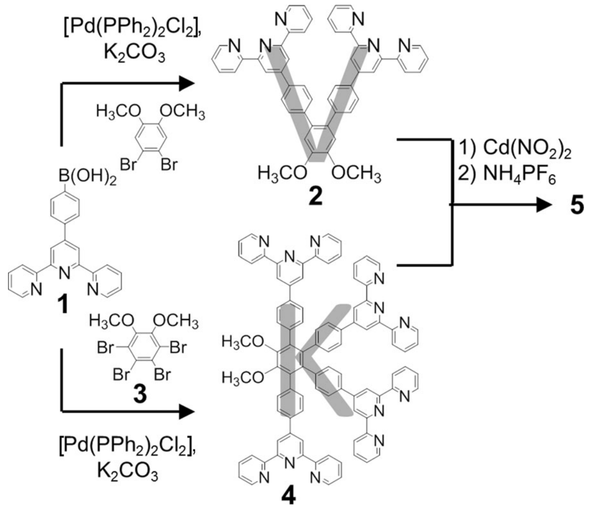


5

Figure 2. Terpyridine-based Sierpiński triangle **5**.



Scheme 1. Synthesis of the key terpyridine building blocks **2** ("V") and **4** ("K").

under an atmosphere of argon.[29] Its ^{1}H NMR spectrum showed the characteristic peak at 3.76 ppm for the installed OCH_3 marker and the presence of two completely different arms (**a** and **b**, Scheme 1). The ^{13}C NMR spectrum showed a peak at 60.76 ppm, which corresponds to the OCH_3 substituents.

All of the proton peaks were assigned using COSY and NOESY NMR spectroscopy. The ^{13}C NMR assignments and the mass-spectrometric data are in full agreement with the ligand structures. The colorless "V" ligand **2** was also synthesized (80%) by a slightly modified procedure[29] from commercially available 4,5-dibromo-1,2-dimethoxybenzene under Suzuki cross-coupling conditions. It was easily characterized by ^{1}H NMR spectroscopy and mass spectrometry. The aromatic region of ligand **2** showed one set of characteristic terpyridine peaks and one set of aromatic phenyl-spacer peaks; a sharp singlet was observed at 4.02 ppm, which corresponds to the OCH_3 markers. The ^{13}C NMR spectrum displayed a peak at 56.40 ppm for the OCH_3 group also.

The facile one-step assembly of Sierpiński triangle **5** (Scheme 1) utilized an exactly 1:1 solution of **2** and **4** in $CHCl_3$ to which a methanolic solution of $Cd(NO_3)_2{\cdot}4H_2O$ (3 equiv) was added. The solution was stirred for 30 minutes at 25°C; then, excess NH_4PF_6 was added to effect counterion exchange to PF_6^-. The desired PF_6 complex precipitated and was filtered and repeatedly washed with MeOH to remove excess NH_4PF_6. Complex **5** was obtained without any further purification as a light yellow solid in > 95% yield.

The Sierpiński triangle **5** was completely characterized by ^{1}H, COSY, and NOESY NMR spectroscopy and ESI and traveling-wave ion mobility (TWIM) mass spectrometry, along with transmission electron microscopy (TEM). The ^{1}H NMR spectrum of **5** showed the characteristic features of a tpy–Cd^{II}–tpy complex, with a sharp and simple pattern being indicative of a discrete structure with a high degree of inherent structural symmetry. The structural simplicity and symmetry were reflected by the ^{1}H NMR spectrum. The imbedded methoxy markers within each ligand appeared in the product as two distinct singlets at 3.98 ppm (from "V") and 3.87 ppm (from "K") with a precise 1:1 ratio, initially supporting the formation of a product that possesses D_{3h} symmetry. Notably, peaks that would be expected for polymeric structures and impurities were not observed. The aromatic region exhibited the peak ratio expected for three different sets of 3′,5′-tpy protons for arms **a**, **b**, and **c** (8.92, 8.91, and 8.74 ppm, respectively; Figure 2 and Figure 3); the downfield shifts resulted from deshielding upon complexation.[28] The 6,6″-tpy protons were noticeably shifted upfield (7.92, 7.68, and 7,80 ppm, respectively, for **a**, **b**, and **c**) when compared with the free ligands,[23] as expected. All of the peaks in the ^{1}H NMR spectrum were assigned and the assignments verified with the aid of 2D-COSY and 2D-NOESY experiments; they are in complete agreement with the proposed structure.

The ^{13}C NMR spectrum of complex **5** exhibits three signals for the different and readily identifiable 3′,5′-tpy

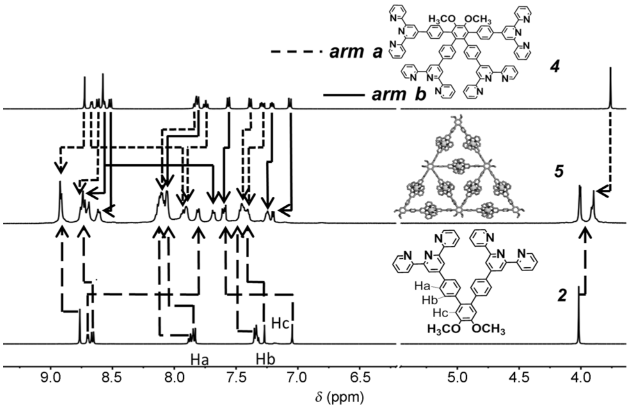


Figure 3. Stacked ^{1}H NMR spectra (500 MHz) of ligands **2** (bottom) and **4** (top) in $CDCl_3$ and of complex **5** in CD_3CN (0.25 mg mL^{-1}; center). Arrows indicate assigned resonance shifts that occur upon complex formation.

carbon atoms at 158.39, 155.32, and 154.93 ppm, respectively, along with two very close, yet distinct peaks for the OCH_3 substituents at 56.02 and 56.00 ppm, which further supports the proposed structure (Supporting Information, Figure S12).

Sierpiński triangle **5** was further characterized by ESI–MS coupled with TWIM mass spectrometry.[22–24,32–36] In ESI–MS (Figure 4), a series of dominant peaks were generated at m/z values of 763.4, 854.2, 965.2, 1103.9, 1282.4, and 1520.3, which correspond to charge states from 11 + to 6 + from the loss of various numbers of PF_6^- anions. The isotope pattern of each peak is in agreement with the corresponding simulated isotope pattern. Additional evidence for formation of the Sierpiński triangle **5** was provided by ESI–TWIM MS (Figure 4); the corresponding spectrum showed a set of single and narrow bands for charge states from 11 + to 6 +, which is in agreement with the presence of one single structure **5**.

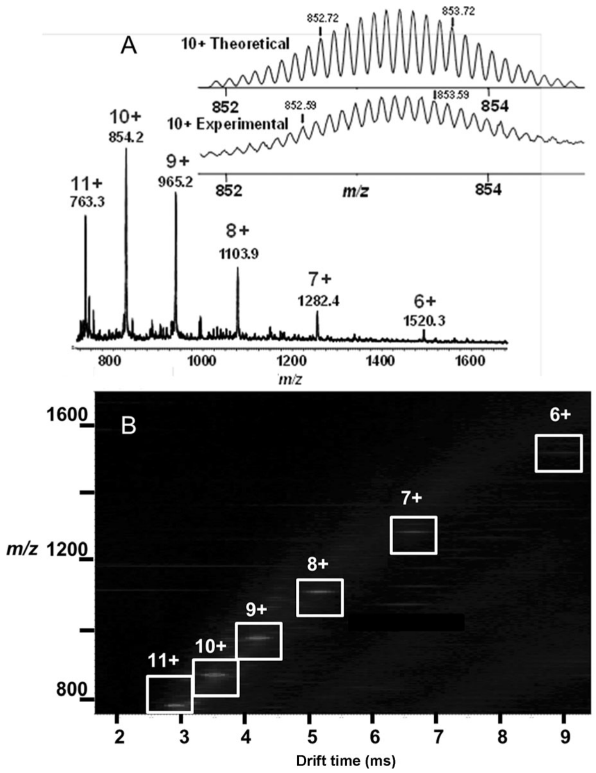


Figure 4. A) ESI–MS and B) 2D ESI–TWIM MS plot of **5**. The charge states of intact assemblies are marked.

The structure of complex **5** was further confirmed by comparison of the experimental collision cross sections (CCSs) of the charge states 11 + to 6 +, which were deduced from their drift times measured by ESI–TWIM MS, with the theoretical CCSs of the complex without any counterions (100 energy-minimized structures obtained by molecular modeling). Experimental and theoretical CCSs of triangle **5** are listed in Table 1.

Table 1: Drift times and collision cross sections for the Sierpiński triangle **5**.

Charge	Drift time [ms]	CCS_{exp} [Å^2]	CCS_{theory} [Å^2]
6+	8.93	1309.2	1388.3
7+	6.49	1295.5	
8+	5.01	1288.7	
9+	4.11	1297.2	
10+	3.40	1288.5	
11+	2.76	1242.3	
average of all charge states		1286.9	

TEM afforded the visualization of the triangle **5**, which revealed a direct correlation of both the size and shape of single molecules upon deposition of a dilute solution (ca. 10^{-5} M) of complex **5** in MeCN with PF_6^- counterions on carbon-coated copper grids (300 mesh). The molecular framework was observed as a uniform dispersion of individual molecules with triangular shape, clear edges, and discernable vertices. The average distance (5.6 nm) between the vertices correlates well with the size obtained from the optimized molecular model (Figure 5).

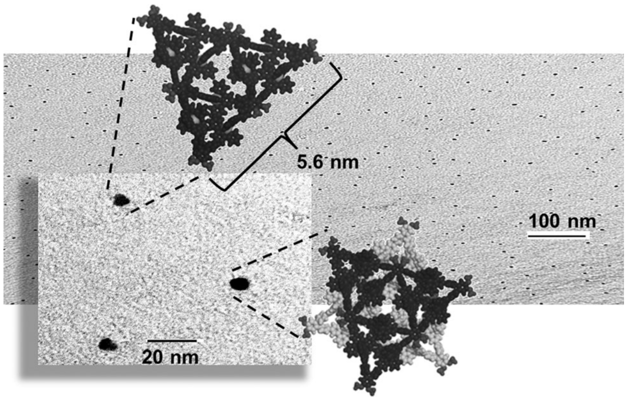


Figure 5. Low-magnification TEM image of the Sierpiński triangle **5** showing a uniform field of particles. The high-magnification TEM image clearly exhibits triangular motifs and a slightly larger and rounded picture of a proposed aggregate (where the two triangles illustrate a potential arrangement). Computer-generated models illustrate the different OCH_3 (singlet markers) environments that were observed in ^{1}H NMR dilution experiments to ascertain the presence of individual versus stacked species.

The TEM image (Figure 5) also suggests that stacking or aggregation occur at higher concentration, where two Sierpiński triangles lie atop each other to generate a "Star of David"-like motif. This phenomenon was supported by ^{1}H NMR experiments, where at higher concentrations, a small extra peak was observed as a shoulder to the peak assigned to the OCH_3 markers of ligand "K"; thus, the NMR spectrum is a combination of stacked (two or more) and individual species. At lower concentrations, a single peak was observed for these markers. The "V" ligand marker signals are unaffected by the concentration (see the Supporting Information for the details of the NMR dilution experiment, Figure S17).

In conclusion, we have achieved the self-assembly of a first-generation Sierpiński triangle with D_{3h} symmetry using tpy–Cd$^{\mathrm{II}}$–tpy connectivities in near quantitative yield through the use of structurally directed, multi-topic 2,2′:6′,2″-terpyridine ligands possessing programmed structural features. NMR spectroscopy, ESI and TWIM mass spectrometry, and TEM provided great insight into the size, shape, symmetry, and molecular structure of the assembled product. The application of ligands with complementary directivity to the assembly of higher-generation structures is currently underway.

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