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Constructing High Generation of Sierpiński Triangles with Molecular Puzzling

Zhilong Jiang,[a,§] Yiming Li,[a,b,§] Ming Wang,[c] Die Liu,[a] Jie Yuan,[a] Mingzhao Chen,[a] Jun Wang,[a] George R. Newkome,[d] Wei Sun,[e] Xiaopeng Li,[b,*] Pingshan Wang[a,*]

Abstract: As a fractal geometry, Sierpiński triangle has attracted increasing attention in science, technology, engineering, math and art. Herein, three generations of metallo-trigonal supramolecular architectures, metallo-triangles, were assembled using terpyridine (tpy) complexes. The first generation (**G1**) of *mono*nuclear metallo-triangle was directly obtained by reacting a 60°-orientated *bis*terpyridinyl ligand and Zn(II) ion. The direct self-assembly of **G2** and **G3** triangles by mixing organic ligands and Zn(II). However, only generated a mixture of **G1** and **G2,** as well a trace amount of insoluble polymer-like precipitate. Therefore, a modular strategy based on the connectivity of <tpy-Ru(II)-tpy> was employed to construct two predesigned metallo-organic ligands for the assemblies of the second and third generations (**G2** and **G3**) of Sierpiński triangles. Metallo-organic ligands, **L**^{A} and **L**^{B}, with multiple uncomplexed free terpyridines, were obtained through Suzuki-cross coupling on the Ru(II) complexes, and then assembled with Zn(II) or Cd(II) to achieve high generations of metallo-trigonal architectures with nearly quantitative yield. **G1**-**G3** architectures were characterized by NMR, ESI-MS, TWIM-MS, NOESY, DOSY and TEM.

As one of the most well-known and versatile fractal figures, Sierpiński triangle was first formulated by a Polish mathematician Waclaw Sierpiński.[1] Up to date, Sierpiński triangle has attracted increasing attention in science, technology, engineering, math and art. In particularly, the recent development of supramolecular chemistry[2-4] and/or self-assembly[5, 6] allows chemists and physicists to explore this fractal geometry at molecular level. Along with theoretical prediction,[7] different generations of Sierpiński triangles have been approached by halogen bonding,[8] hydrogen bonding[9] and coordination[10-12] in ultrahigh vacuum using surface self-assembly. However, constructing discrete generation of Sierpiński triangle instead of mixture still remains a challenge in surface self-assembly.

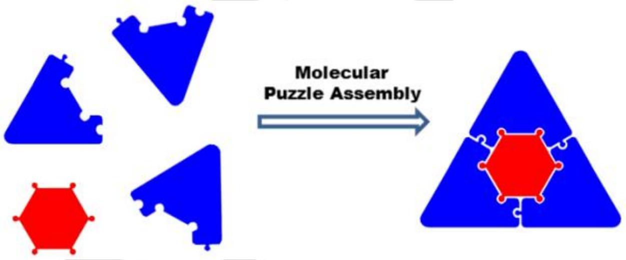

Figure 1. Illustration of the molecular assembly based on a puzzling strategy.

Coordination-driven supramolecular chemistry[13-26] in solution may provide an alternative approach to achieve different generations of Sierpiński triangles in a precisely-controlled manner. Indeed, Newkome and coworkers reported a terpyridine (tpy) based molecular Sierpiński metallo-triangle **G2**, which was assembled based on a 60º-oriented bisterpyridine (**V**) and 1,2,3,4-*tetra*terpyridine (**K**) and Cd(II).[27] In the exploration of next generation Sierpiński triangle, however, the generation of undesired low generation of triangles or coordination polymers by self-sorting of individual ligands cannot be avoided through simple stoichiometry control in the multicomponent self-assembly.

In tpy-based supramolecular chemistry, it is well-documented that Ru(II) and Fe(II) possess stronger coordination with tpy than Cd(II) and Zn(II).[28-32] Moreover, <tpy-Ru^{2+}-tpy> connectivity with remarkable stability is able to tolerate the harsh chemical process, for example, high temperature, basic condition, column chromatography etc. With regard to application, Ru(II)-tpy complexes have been extensively studied dye-sensitized solar cell,[33,34]. Unfortunately, <tpy-Ru(II)-tpy> connections were seldom used to assemble large and complex supramolecular architectures because of absence of selectivity and reversibility. We herein report the construction of different generations (**G1** to **G3**) of Sierpiński triangles using the combination of Ru(II) and Zn(II) or Cd(II) in a step-wise approach.[28,30,35-39] In the first step, metallo-organic ligands based on <tpy-Ru(II)-tpy> connectivity were designed and synthesized as the building blocks with enhanced selectivity and specificity. In the second step, these building blocks were assembled with Zn(II) or Cd(II) through highly reversible coordination to form large architectures as molecular puzzling (Figure **1** and Scheme **1**). Such molecular puzzling is reminiscent to the specificity of an enzyme based on the structural and conformational complementarity between enzyme and substrate.

In our initial study, Zn(II) was used to replace Cd(II) in the self-assembly of **V** and **K** with a precisely stoichiometrical ratio (**V**: **K**: Zn = 3 : 3 : 9) according to previous study.[27] However, a mixture of the Sierpiński triangle **G2** $[\mathbf{Zn_9V_3K_3}]^{18+}$ and small

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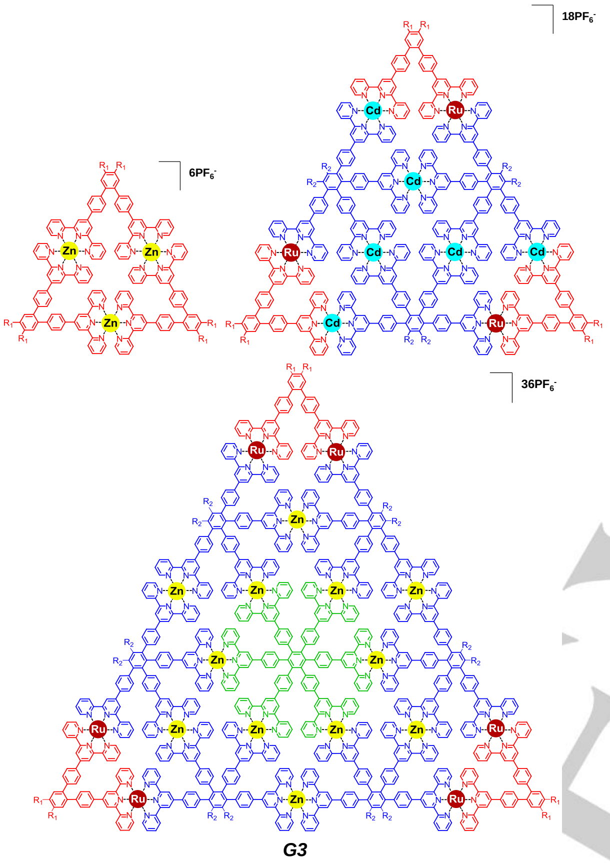
[a] Dr. Z. Jiang, Y. Li, Dr. D. Liu, J. Yuan, M. Chen, Prof. Dr. P. Wang
College of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan-410083, China
E-mail: chemwps@csu.edu.cn
[b] Y. Li, Prof. Dr. X. Li,
Department of Chemistry, University of South Florida, Tampa, Florida 78666, United States
E-mail: xiaopengli1@usf.edu
[c] Prof. Dr. M. Wang
State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, Jilin-130012, China
[d] Prof. Dr. G. R. Newkome
Departments of Polymer Science, Maurice Morton Institute of Polymer Science, Department of Polymer Engineering and Chemistry, The University of Akron, Akron OH-44325, United States
[e] Prof. Dr. W. Sun
College of Mineral Processing and Bioengineering, Central South University, Changsha, Hunan-410083, China

[§] Those authors contributed equally to this work.

metallo-triangle **G1** [$\mathbf{Zn_3V_3}$]$^{6+}$ was generated due to the self-sorting of **V** with Zn(II). All attempts to obtain **G2** as the single assembly proven unsuccessful even after numerous adjusting the sequence of the addition, reaction temperature, time, solvents and counterions (Scheme S3 and Figure **2**, and also see Electronic Supporting Information, ESI). We speculated both triangle **G2** [$\mathbf{Zn_9V_3K_3}$]$^{18+}$ and small metallo-triangle **G1** [$\mathbf{Zn_3V_3}$]$^{6+}$ might possess the similar thermodynamic stability and entropy favored effect.



Scheme 1. Chemical illustration of three Sierpiński triangles **G1**, **G2** and **G3**.

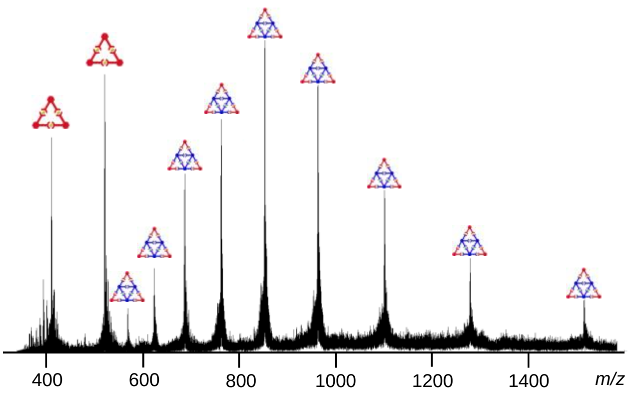
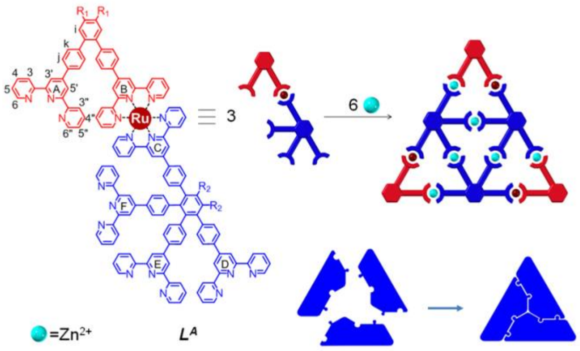


Figure 2. ESI-MS of a mixture of **G1** and **G2** by direct self-assembly of **V**, **K** and Zn(II).

In order to avoid the formation of small metallo-triangle **G1**, it is necessary to prevent from the self-sorting of **V** and metal ion alone. Based on geometrical analysis of the structure, a molecular puzzling strategy was utilized to re-design the synthetic pathway, or the step-wise approach with metallo-organic ligand. This strategy can certainly circumvent the self-sorting coordination when the assembly including multiple components owing to the high specificity and selectivity of metallo-organic ligand. In principle, the self-sorting of individual ligand could be blocked if **V-** and **K-**shaped *poly*terpyridinyl ligands were linked with Ru(II) ion to obtain a <tpy-Ru(II)-tpy> complex moiety [**V**-Ru(II)-**K**] or $\mathbf{L^A}$ (Scheme **2**). In the presence of Zn(II), the self-assembly of Sierpiński triangle **G2** should be formed as the sole structure. The directly reacting **V**, **K** and $RuCl_3$ in 1:1:1 stoichiometry ratio only produced a mixture of Ru(II)-complexes which are hard to separate the target one because of the closed polarity.

Thanks to the stable <tpy-Ru(II)-tpy> connectivity in Pd-based catalyzed reaction and column chromatography, $\mathbf{L^A}$ was prepared with 7-step reactions starting from 2-methoxyphenol (Scheme S1). The target metallo-organic ligand $\mathbf{L^A}$ (42%) was obtained by a final 3 folds of Suzuki coupling reaction with 4-terpyridinyl-B(OH)$_2$ using Pd^0 as a catalyst after column separation (Al_2O_3, $CHCl_3$/MeOH). The asymmetrical $\mathbf{L^A}$ contained four uncomplexed free tpys, which could be used as multiple junctions during the next step assembly. In the ^{1}H NMR spectrum of $\mathbf{L^A}$ (Figure **3**A), two singlets at *ca.* 9.1 and 9.3 ppm were assigned to the tpy$H^{3',5'}$ of <tpy-Ru^{2+}-tpy> moieties; four singlets of uncomplexed tpy$H^{3',5'}$ exhibited at *ca.* 8.6-8.8 ppm. Other peaks related to the complexed and uncomplexed terpyridines, also the methyl and alkyl groups were fully assigned according to the ^{1}H/^{13}C NMR and 2D-NOE NMR spectra (Figure **3**A and ESI). The HR-MS spectrum of $\mathbf{L^A}$ (Figure S47 in ESI) indicated two clear peaks of m/z = 1145.30 and 763.85 corresponding to [$\mathbf{L^A}$-2PF$_6$]$^{2+}$ and [$\mathbf{L^A}$$\mathbf{H}^+$-2PF$_6$]$^{3+}$, respectively.

The assembly of a *di*nuclear Sierpiński triangle **G2** (Scheme **2**) was carried out with Zn(II) and metallo-organic ligand $\mathbf{L^A}$ in MeOH/$CHCl_3$. After counterion exchange with excess NH_4PF_6, the precipitate was washed with D. I. water and MeOH to remove the excess NH_4PF_6, the pale red powder of molecular Sierpiński triangle **G2** was obtained (>95%). As expected, $\mathbf{L^A}$ prevented from the self-sorting of **V** and **K** individually with metals, as well the random connections between **V**, **K** and metals.



Scheme 2. The synthetic route of supramolecular Sierpiński triangle **G2**.

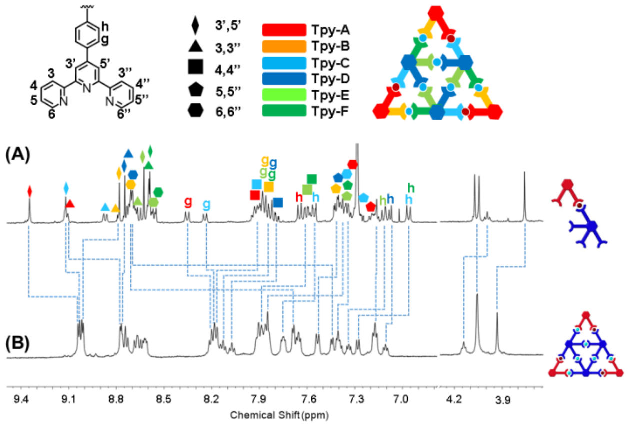


Figure 3. ^1H NMR (500 MHz) of (A) metallo-ligand L^A in $CDCl_3$ and (B) Sierpiński triangle **G2** in CD_3CN.

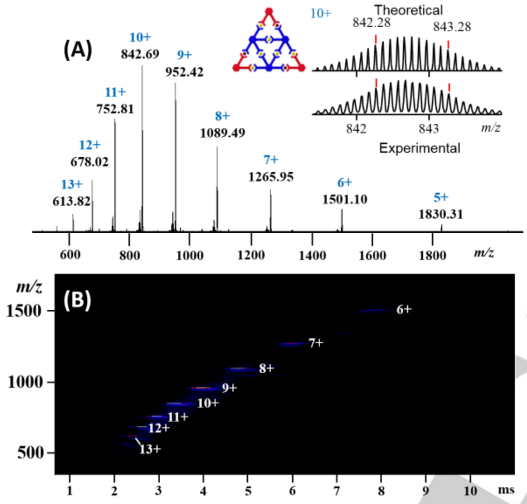
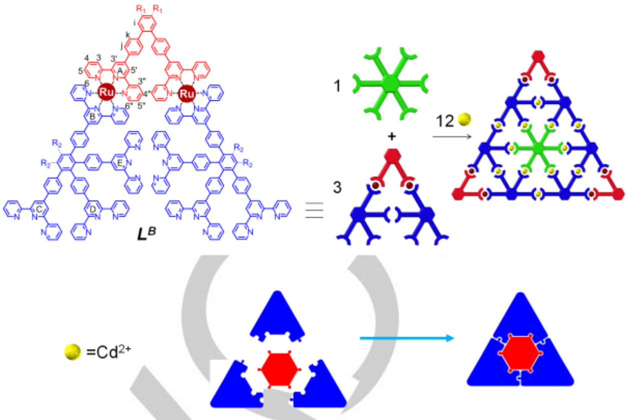


Figure 4. (A) ESI-MS and (B)TWIM-MS spectra of Sierpiński triangle **G2**.

The structural characterization was first performed with ^1H NMR and 2D-NOESY spectroscopies (Figure **3**B). Compared with L^A, the protons of <tpy-Ru(II)-tpy> for assembled **G2** clearly showed the chemical shifts as the coordinated <tpy-Zn(II)-tpy> derived from the uncomplexed tpys shifted downfield except the protons of tpy$H^{6,6''}$ positon after coordination with Zn(II). Some protonic signals of the pyridine rings were overlapped after assembling; nevertheless, the two sets of terpyridinyl peaks, *i.e.*, <tpy-Ru(II)-tpy> and <tpy-Zn(II)-tpy> moieties, could be validated accurately through 2D-COSY and 2D–NOESY NMR spectra. The singlets of CH_3O- and triplet of $–CH_2O$- implied the formation of a single molecular Sierpiński triangle **G2**. The 2D-DOSY NMR spectrum for **G2** (Figure S29) displays a single diffusion band indicating that a discrete component was assembled solution and no other by-product and oligomer co-existed. The diffusion coefficient of $2.24x10^{-10}$ m^2s^{-1} at 298 K also showed that the experimental hydrodynamic radius (r_H=2.66 nm) was consistent with the calculated molecular radius (r_m=2.65 nm).[42]

The ESI-MS and TWIM-MS data (Figure **4**A) further undoubtedly convinced the metallo-architecture of **G2** with high purity. The ESI-MS (Figure **4**A) revealed a series of peaks with the charge states of 13+ to 5+ from successive loss numbers of PF_6^-. The experimental *m/z* values and isotope patterns for each charge state were consistent excellently with the respective calculated values of molecular weight at 10159 Da. Additional evidence was provided by ESI-TWIM-MS experiments (ESI-MS coupled with traveling-wave ion mobility spectrometry),[42-45] each charge states of 14+ to 6+ (Figure **4**B) showed a single band with a narrow drift time distribution which excluded the existence of other isomers or components.



Scheme 4. Chemical illustration of synthetic route of supramolecular **G3**.

In the exploration of Sierpiński triangle **G3** with *hexa*terpyridine **H** as the center fitting, direct self-assembly of **V**, **K**, **H** and metals in a precisely stoichiometrical ratio of 3:6:1:18 also generated a mixture of small metallo-triangle **G1** $[Zn_3V_3]^{6+}$ derived from self-sorting of **V** and Zn^{2+}, Sierpiński triangle **G2** $[Zn_9V_3K_3]^{6+}$, as well an insoluble polymer-like solid which should be caused from a multicomplexition of *poly*terpyridines and Zn(II) (Figures S4 and S43). According to the structural and conformational complementarity, metallo-organic ligand L^B (Scheme **4**) was designed as the key intermediate in the molecular puzzling with *hexa*terpyridine ligand **H**. The synthesis of L^B was accomplished with a similar synthesis procedure of L^A. After a tribromoterpyridine-Ru(II) mono-capping adduct $Br_3TpyRuCl_3$ (Scheme S2 in ESI) reacting with a 60^o-angle orientated *bis*terpyridine **V** in a stoichiometrical ratio of 2.1:1, the obtained brominated metallo-complex was conducted with a final six-folds Suzuki-coupling reactions with 4-terpyridinyl-$B(OH)_2$ using Pd^o as the catalyst under argon. A purified product L^B (62%) was acquired through the column chromatography (Al_2O_3, 200-300 mesh eluting with $CHCl_3$/MeOH). The ^1H NMR spectrum of L^B obviously showed two singlets at 9.03 and 9.45 ppm attributing to two kinds of complexed tpy$H^{3',5'}$, as well three singlets of uncomplexed tpy$H^{3',5'}$. Another strong evidence was raised from the two singlets for $–OCH_3$ and one ternary peak for $–OCH_2$- at *ca.* 3.2-4.0 ppm with the exactly integration ratio of 3:2:3. The further validation of the L^B was achieved by 2D-NOESY NMR spectra and ESI-MS (Figure S35 and S36 in ESI), all data were consisting with the theoretical and expected values.

The assembly of Sierpiński triangle **G3** was carried on in $MeOH/CHCl_3$ (1:1) by adding Cd^{2+} solution (MeOH) drop-wise to L^B slowly. After exchanging the counterion to PF_6^- with excess NH_4PF_6, the precipitate was washed with H_2O and MeOH, and the final **G3** was collected as pale red powder (>95%).

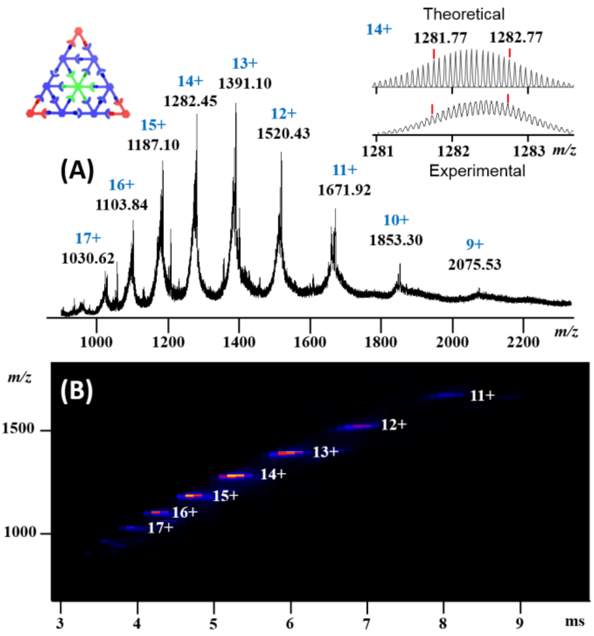


Figure 5. (A) The ESI-MS and (B) TWIM-MS spectra of **G3**.

The assembled architecture **G3** was fully characterized by ^{1}H NMR, 2D-NOESY, ESI-MS and TWIM-MS. After complexation with L$^{\mathbf{B}}$, the ^{1}H NMR peaks (Figure S39) at aromatic region exhibited the broad and overlapped signals due to the large size and multiple sets of aromatic rings. Nevertheless, three aliphatic peaks indicated two singlets for –OCH_3 and one triplet for –OCH_2- could interpret the assembly. The diffusion-ordered NMR spectroscopy (DOSY) spectrum (Figure S42) displayed a distinct single band with the diffusion coefficients of 1.58x10^{-10} m^2s^{-1} at 298 K; the experimental hydrodynamic radius (r_H=3.77 nm) was consistent with the calculated molecular radius (r_m=3.83 nm), recommending the construction of a discrete single molecular structure. ESI-MS and TWIM-MS measurements were used further to validate the architecture **G3**. As shown in Figure **5**A, ESI-MS spectrum of **G3** revealed a series of peaks the charge states from 18+ to 10+ derived from losing corresponded PF_6^-, a single and narrow signals on the 2D TWIM-MS plot (Figure **5**B) suggested a single architecture. The experimental *m/z* values and isotope patterns for each charge state are consistent well with the respective theoretical molecular weight at 19980.99 Da.

Transmission electron microscopy (TEM) experiments were facilitated visualization of morphological **G2** and **G3** (Figure **6**), revealing directly both the size and shape of individual molecules upon deposition of a dilute (~10^{-7} M) MeCN solution of Sierpiński trianglar samples on carbon-coated grids (Cu, 400 mesh). The outline of triangular shaped patterns located on the film with edges and corners can be observed. The average lengths (5.9 and 8.6 nm, respectively) of the two edges of **G2** and **G3** perfectly fit the size that was obtained from the optimized molecular modeling. The UV-vis absorptions and fluorescence spectrum were also evaluated (Figures S50 and S51).

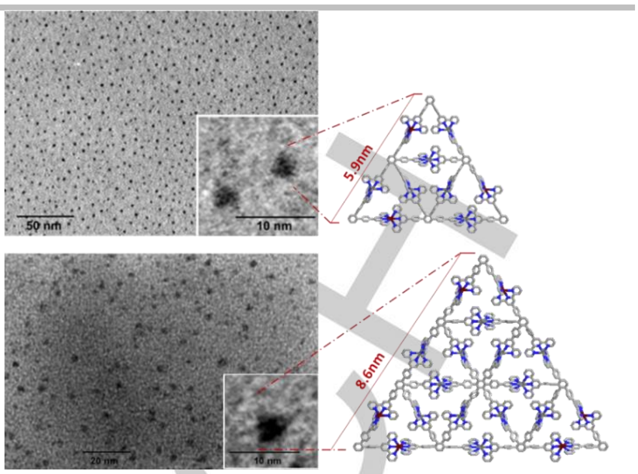


Figure 6. TEM images and energy-minimized structures of Sierpiński triangle **G2** (Upper) and **G3** (Bottom).

In summary, different generations of metallo-architectures with the geometry of Sierpiński triangle were designed and assembly based on the structural and conformational complementarity of building blocks, or molecular puzzling. The stepwise strategies were employed to overcome the formation of undesirable metallo-supramolecules and coordination polymers. The key intermediates, metallo-organic ligands, were obtained through the Pd^{o} catalyzed multiple Suzuki cross-coupling on brominated <tpy-Ru(II)tpy> complexes with high specificity and selectivity. It is expected that this molecular puzzling strategy will allow us to create more complicated fractal architectures with desired shapes, sizes and functionality.

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Conflict of interest

§Those authors contributed equally to this work.

The authors declare no conflict of interest.

Keywords: terpyridine, self-assembly, modular strategy, Sierpiński triangular, supramolecular chemistry

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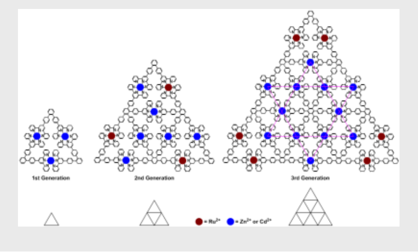
Layout 1:

COMMUNICATION

Molecular Sierpiński triangle assembled from the rigid, puzzle-like metallo-organic ligands



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Constructing High Generation of Sierpiński Triangles with Molecular Puzzling