Symmetrically Backfolded Molecules Emulating the Self-Similar Features of Sierpinski Triangle†

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We have synthesized self-similar molecules (G3 and G2; based on phenylalkynyl backbones) with symmetrically backfolded shapes inspired by the famous fractal of the Sierpinski triangle. Unlike the more traditional, starburst dendrimers, the centripetal-shaped Sierpinski molecules feature side branches symmetrically bent away from the growth direction of the main branch, thus contrasting the natural-tree shape. Molecule G3 exhibits three distinct levels of structural hierarchy comprising the primary, secondary and tertiary branches, while the smaller G2 contains only features of the 1st and 2nd orders. In spite of the much larger conjugated backbone of G3, its UV-vis absorption remains little shifted in wavelength compared to G2, while the emission of G3 is curiously blue-shifted by over 50 nm from that of G2.

The relevance of the mathematically famous fractal of the Sierpinski triangle to molecular design is illustrated in Fig. 1. The hierarchy (or iteration) of the triangles is superimposable with a ternary tree that features a symmetrically backfolded geometry,1 in which the subbranches are bent away from the pointing direction of the main branches. Such a backfolded geometry contrasts with the starburst shape of conventional dendrimers, with all branches in the latter radiating away from the center (e.g., H4L3; Fig. 1), mimicking the growth direction of a biological tree. Even though symmetrically backfolded molecules have been studied by chemists (e.g., L1 and L2 in Fig. 1 and other examples2), most examples remain rather simple systems consisting of only primary and secondary branches (e.g., L1 and L2). The synthesis of Sierpinski molecules of higher iterations (e.g., G3 in Fig. 2, with three generations of branches) has not been reported.

The lack of synthetic efforts on higher-generation Sierpinski molecules is curious, and stands in sharp contrast not only with the numerous reports on conventional dendrimers of the radiating, starburst shape,3 but with the growing numbers of supramolecular assemblies related to the Sierpinski fractal.4 On

Fig. 1 Two backfolded molecules (L1 and L2), the starburst dendrimer H4L3, and a Sierpinski triangle (with the equivalent ternary tree shown in red). L2 resembles the Sierpinski triangle, whereas H4L3 has a radiant, geometrically different form. The backfolded molecules (L1 and L2) can be deconstructed into tritopic subunits attached to the inner fragments (shown in green).

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Fig. 2 A schematic model of molecule G3: a self-similar Sierpinski molecule featuring two carboxylate ester groups at the primary branch, together with six ester groups and 8 thioether groups at the secondary and tertiary branches, respectively.

of starburst units (e.g., the regular tritopic unit; see also L1 and L2 in Fig. 1); and the resultant networks, in spite of their unusual complexity, can be deconstructed into subnets corresponding to the starburst units of the molecule.5

To fill in the gap in the study of higher-generation Sierpinski molecules, and to draw more attention to this unconventional class of self-similar molecules, we here report the synthesis and characterization of molecule G3 (Fig. 2). G3 was designed with consideration to synthetic feasibility and functionality. For example, a total of six long alkyl groups (i.e., n-decyl, n-C10H21) were installed at the (two) primary and (four) secondary termini to improve solubility; and extra phenylacetylene spacer units are built into the primary and secondary branches to alleviate steric hindrance. Also, the large, conjugated phenyleneacetylene backbone might help future studies on how the Sierpinski shape impacts photophysical properties (e.g., fluorescence/exciton lifetime, charge/energy transfer). In addition, the eight thioether groups at the G3 branches can serve as metal-binding sites; while the long, floppy alky chains might also impart liquid crystal properties in combination with the rigid Sierpinski backbone.

The synthesis of G3 builds on a convergent strategy extensively utilizing the well-established Sonogashira reaction,6 in conjunction with the masking/demasking of the iodo and terminal alkynyl groups by means of the triazene7 and the trimethylsilyl (TMS) groups, respectively.8 Among the many precursors, molecule 9 is a cornerstone for the overall assembly scheme. As shown in Fig. 3, the synthesis of 9 begins with a carboxylic acid (2) formation from 3,5-dibromo-4-iodobenzenitrile (1), followed by esterification with 1-decanol to give 4 in 80% yield (via the acid chloride 3). Sonogashira cross-coupling of 4 with 1 equivalent of trimethylsilylacetylene (TMSA) selectively displaces the iodo group to provide 5 in 76% yield, indicating that the higher reactivity of the iodo group overrides the steric hindrance from the flanking Br atoms. The two Br groups in 5 were then reacted with 2 equivalents of 4-triazenephenylacetylene (S4, see Fig. S1 for its preparation) at 90 °C to afford compound 6 in 60% yield. After unmasking the TMS group of 6 with tetrabutylammonium fluoride (TBAF), the resultant terminal alkynyl compound 7 was coupled with the iodo compound S5 to afford 8 in 56% yield. Heating 8 in methyl iodide at 120 °C in a sealed vessel then replaces the triazene units by the iodo groups, generating 9 in 75% yield.

With the key precursor 9 in hand, the assembly of G3 becomes relatively straightforward, which involves installing the tertiary branches and a Glaser coupling that oxidatively homocouples the terminal alkyn (Fig. 4). Specifically, molecule 11 was prepared by coupling 4-ethynylthioanisole (S8) with the above-mentioned molecule 5 (followed by the removal of the TMS group to recover the terminal alkyn function, with overall yields over 60%). Subsequently, 11 was subjected to a Sonogashira coupling with 9 to generate the precursor 12. Notice however that the reaction between 11 and 9 required the rather stringent conditions of refluxing for 40 h, and the yield was modest (37%). Finally, compound 12 (without removing the TMS group) directly underwent a homocoupling reaction in the presence of CuCl in N,N-dimethylformamide.

Fig. 3 The synthetic steps for molecule 9.

Fig. 4 Synthetic steps for G3 and G2 (R is an n-decyl group: n-C10H21).
(DMF) to afford the target compound G3 as an orange solid in 52% yield.

The product G3 was extensively characterized, e.g., by solution 1H NMR, 13C NMR, 2D COSY, DEPT spectra and cyclic voltammetry (Fig. S2 and elsewhere in ESI). In addition, high-resolution mass spectrometry HRMS found, e.g., 3478.4020 (100%) for M + H+ (3478.435 calculated for C234H218O12S8 + H+), and the CHN elemental analysis results are also consistent with the proposed structure, i.e., calculated for C234H218O12S8: C, 80.79; H, 6.32; found: C, 80.42; H, 6.57.

For comparison, the lower generation Sierpinski molecule G2 was also synthesized (see ESI for the procedure and the single crystal structure, Fig. S3). A comparison of the solution UV-vis absorption and emission spectra of G2 and G3 (Fig. 5) unveils some surprises. The UV-vis wavelengths of maximum absorption (λmax) of conjugated systems generally arise from π→π* transitions from the HOMO to the LUMO, and often red-shift significantly with added conjugation. In spite of the much larger π-electron backbone of G3, its λmax is, surprisingly, only slightly red-shifted relative to that of G2 (with λmax,G2 = 329 nm and λmax,G3 = 324 nm). A bathochromic side band (most likely from π→Π* transitions) was also observed for both G3 and G2. Here the surprise is more acute: the absorption edge for the smaller G2 is red-shifted relative to the larger conjugated G3. Unexpected observations continue in the fluorescent spectra. In THF solutions, the small G2 emits at wavelengths (λmax=520 nm) much longer than G3, which exhibits a relatively sharp emission at 431 nm and a broader emission at 463 nm. In the solid state, both G2 and G3 are red-shifted (λmax,G2 = 530 nm; λmax,G3 = 495 nm), with the smaller-size G2 continuing to fluoresce at significantly longer wavelengths than its more conjugated congeners G3. The optical blue shifts observed in G3 therefore runs counter to the general trend of higher-generation dendrimers to absorb and emit at longer wavelengths—albeit to a lesser degree for meta-conjugated systems. We suspect that the diacetylene bridge in G2 offers an efficient push-pull pathway between the sulfur and the carboxyl groups to facilitate π-electron delocalization, while such a push-pull effect becomes weaker in the longer, zigzag path offered by G3 (see Fig. S4). It is clearly worthwhile to further probe the ground and excited state dynamics of Sierpinski molecules as such, in order to better account for the unexpected optical blue shifts observed in G3, and to uncover other interesting photophysical properties thereof.

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Notes and references


