

Synthesis and Electrochemistry of Nanometer-Scaled Molecular Dumbbells

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There is great current interest in the synthesis of nanoscopic structures, especially for applications in materials chemistry.¹ Our interest in this field has been to develop a method for preparing discrete nanometer-scaled molecules.² An example is the molecular line in Figure 1, **BABAB**, an oligoimide which has a length of 4.4 nm. As a separate study we have investigated the materials chemistry of certain dendrimers. An example is a poly(amidoamine) modified with naphthalene diimide **A**, which was converted to an electrical conductor by one-electron reduction of the **A** groups on the periphery of the molecule.³ In the present study, we combine these two interests and prepare some unusual molecules in which two dendrimers are connected by rigid rod oligoimides to make dumbbell-shaped molecules. Because the imide groups can be reduced and the periphery of similar dendrimers can be functionalized, this approach will provide unusual molecular structures for study of electrical and optical properties. Because the rigid rods accurately space the polymers we have a method for the synthesis of nanoscale organic structures. Measured along the rod axis, with the arms of the dendron fully extended, the largest molecule prepared in this study is 9.6 nm from end to end.

The idea of building a nanoscale chemistry using dendrimers has been expostulated by Tomalia,⁴ and organized structures composed from aggregated dendrimers have been found.⁵ A number of interesting moieties have been placed between two or more dendritic polymers, including electroactive organometallic

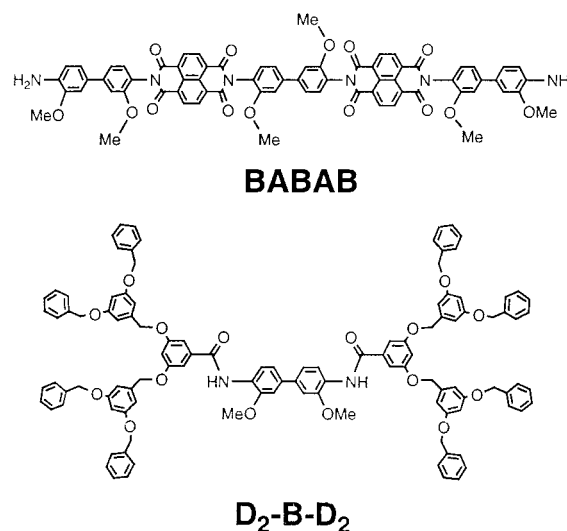


Figure 1. Molecular line and generation 2 dumbbell.

species⁶ and oligothiophenes.⁷ In this latter case the oligomer was not a rigid rod, so the spacing was not well-defined.

Our approach to the synthesis of nanoscopic dumbbells involved coupling amine-terminated oligoimides to monocarboxylic acid dendritic poly(benzyl ethers)⁸ (dendrons), **D₁-CO₂H**,⁹ **D₂-CO₂H**, and **D₄-CO₂H**. The approach (see Supporting Information) is illustrated in Scheme 1 for the largest dumbbell. In initial experiments, these dendrons were coupled to dimethoxybenzidine (**B**), using hydroxybenzotriazole and diisopropylcarbodiimide as coupling promoters, giving **D₁-B-D₁**, **D₂-B-D₂**, and **D₄-B-D₄**. **D-BAB-D** dumbbells were prepared either by coupling 2 equiv of **D-CO₂H** with **BAB**,² or excess **D-B** with naphthalene dianhydride. **D₂-BABAB-D₂** and **D₄-BABAB-D₄** were prepared by coupling excess **D₂-B** or **D₄-B** with **ABA**² at 130 °C with zinc acetate catalysis. Chromatography on silica using ethyl acetate/methylene chloride followed by THF/methylene chloride allowed the side products to elute first, followed by the dumbbells, which were isolated in 40–50% yield. ¹H NMR spectra with the correct peak positions and integrations, and MALDI mass spectra which gave the correct molecular ion verified the structures. The solubility of molecules with rigid rods is always a concern, and we note that the dumbbells, even **D₂-BABAB-D₂**, which has small dendrimers on a long rod, are soluble in solvents such as chloroform.

It is known that the diimide unit represented by **A** can be easily reduced to its radical anion (**A⁻**) and

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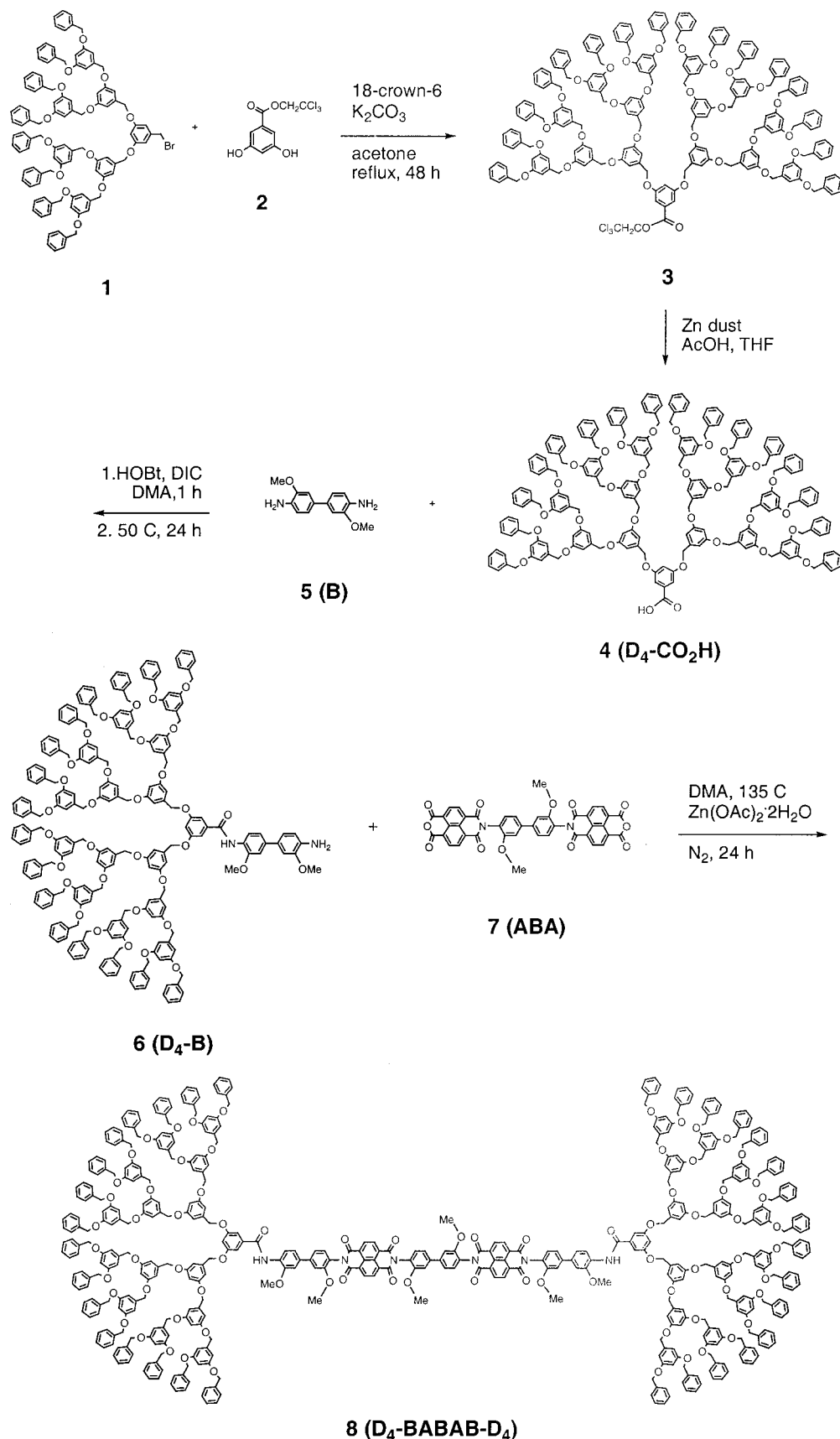
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Scheme 1. Generation 4 Dumbbell Synthesis



dianion (A^{2-}) and that the radical anion is stable even in water. This and other aspects of the anion radical chemistry¹⁰ make the electrochemistry of the dumbbells of some interest. We report initial results on **D₄**-

BABAB-D₄. Cyclic voltammetry in deoxygenated DMF, Bu_4NBF_4 at a glassy carbon disk electrode showed two

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reversible reductions ($\Delta E_p = 70$ mV, $i_p^a/i_p^c = 1$, i_p^c is linear with square root of sweep rate), with apparent E° -0.51 and -1.06 V vs SCE. These values are nearly identical to those for other compounds containing **A** moieties.² Coulometric reduction showed that two electrons/molecule were passed at -0.6 V (one electron/A) generating the bisanion radical (λ_{\max} 782, 702, 605, 473 nm). At -1.1 V two more electrons/molecule gave the tetraanion (λ_{\max} 626, 570, 422, 397 nm). At sweep rates up to 100 V/s there was no evidence that the dendrimer inhibited electron transfer. The diffusion coefficient of **D₄-BABAB-D₄** was estimated by cyclic voltammetry and chronocoulometry as 6.8×10^{-7} cm²/s. A model monomeric compound gave 3.9×10^{-6} .

There are a number of reports of electrochemical reactions of organometallic species which are inhibited when these species are incorporated as the core of a dendrimer.⁶ A presumptive reason is that the surrounding polymer prevents access of the redox site to the electrode surface. The present results contrast with these reports. We note two possible differences: (1) In

the present case, the rigid rod spaces the dendrons further apart allowing more ready access to the central redox site. (2) The organometallic redox chemistry may be somewhat slower than that for **A** diimides and therefore more sensitive to steric blocking by the surrounding polymeric matrix.

Future work will generate even larger molecules and will explore their optical and electrical properties more deeply. Of interest, for example, will be dumbbells with different dendrimers on either end.

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Supporting Information Available: The approach to and full experimental details for the compounds discussed in this communication. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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