Redoxactive Phenylacetylene Monodendrons: Rapid Solid-Phase Synthesis and Their Electrochemical Properties

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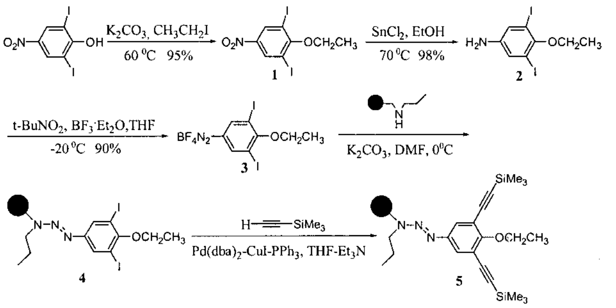
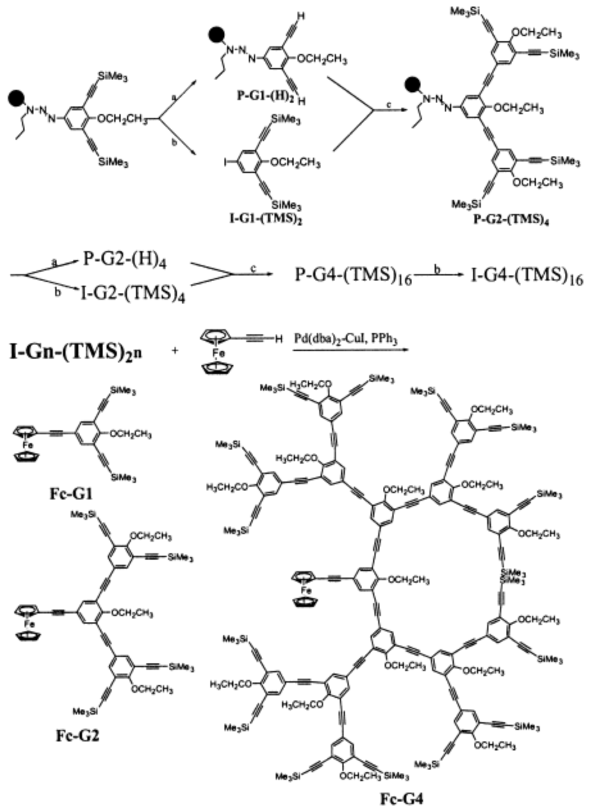
Recently, conjugated dendrimers have found potential applications in electroluminescent devices, thin-film transistors, NLO materials, and artificial photosynthesis.[1−4] However, improvement of their synthetic approach and further understanding of their intramolecular electron or energy transfer process are still required to fulfill the above applications.[5] As to the synthesis of dendrimer, there are two fundamental synthetic strategies.[6] (i) The divergent approach in which one branching unit after another is attached to the core molecule step by step until the steric effects prevent further reactions of the end groups. Advantages of the approach are the rapid growth of the dendrimer series and the increase in mass of isolated products without significant steric inhibition at early generations. (ii) The convergent approach takes the reverse course. The skeleton is constructed stepwise from the end groups toward the inside and finally treated with a multifunctional core molecule to yield the dendrimer. This approach offers such features as involvement of a very small number of reactive sites for growth and the feasibility to dramatically change molecular architecture by using different cores for a given monodendron. In both strategies the number of end group grows exponentially. However, problems usually occur in the divergent approach from the possibility of molecular imperfections at higher generations by the incomplete reaction of the end groups, which will accumulate with the increase of generation. In the convergent one, it is usually difficult to construct higher generation due to the steric problems arising from the reaction of segments and the core molecule. Another major problem in both approaches is the repeated and time-consuming purification process. Solid-supported[7] iterative divergent/convergent synthetic strategy, fulfilling both the rapid exponential growth of length and convenient purification, has been proved to be the most efficient approach for the synthesis of molecular wires.[8] In this communication, this synthetic strategy was introduced to prepare phenylacetylene dendrimers,[9,7b] more specifically, monodendrons, a kind of asymmetric dendrimers which can be easily functionalized at the core and/or periphery site with different electroactive or photoactive components.[10] Therefore, further understanding of their electron or energy transfer process becomes possible.

The Merrifield's peptide resin-supported monomer was prepared according to Scheme 1. 2,6-Diiodo-4-nitrophenol was transformed into potassium salts with K_2CO_3 in acetone, and 3,5-diiodo-4-ethoxylnitrobenene (**1**) was prepare by addition of ethane iodide in 95% yield. The nitro group in compound **1** was reduced into amino group by reacting with $SnCl_2{\cdot}2H_2O$ in alcohol at elevated temperature, and 3,5-diiodo-4-ethoxylaniline **2** in 98% yield was obtained. Reaction of compound **2** with $BF_3{\cdot}Et_2O$ and *tert*-butyl nitrite at −20 °C gave (3,5-diiodo-4-ethoxyl)diazonium tetrafluoroborate (**3**) in 90% yield. The resulting diazonium tetrafluoroborate salt reacted with *n*-propylaminomethyl polystyrene[11] in basic conditions like K_2CO_3 in DMF to give the polymer-supported diiodo compound, **4**. Finally, the Heck−Cassar−Sonogashira−Hagihara reaction[12] of compound **4** and excessive trimethylsilylacetylene in the presence of $Pd(dba)_2$−CuI−PPh_3 gave the polymer-supported monomer **5**.

Scheme 1. Synthesis of Polymer-Supported Monomer 5



Scheme 2. Synthesis of Phenylacetylene Monodendrons by an Iterative Divergent/Convergent Approach and the Synthesis of Redox-active Monodendrons: (a) TBAF, THF, rt; (b) MeI, 115 °C; (c) $Pd(dba)_2$−CuI−PPh_3, 2:1 (v/v) NEt_3/THF, 70 °C.



As Shown in Scheme 2, the starting monomer **5** was divided into two portions. The trimethylsilyl group in

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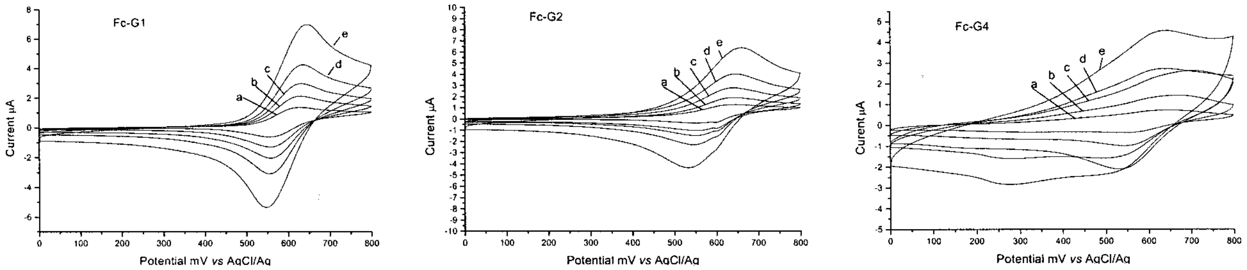

Figure 1. Cyclic voltammograms for 1 mM **Fc-G1**, **Fc-G2**, and **Fc-G4** in CH_2Cl_2 with tetrabutylammonium hexafluorophosphate as supporting electrolytes at a scanning rate of 20 (a), 50 (b), 100 (c), 200 (d), and 500 mV/s (e).

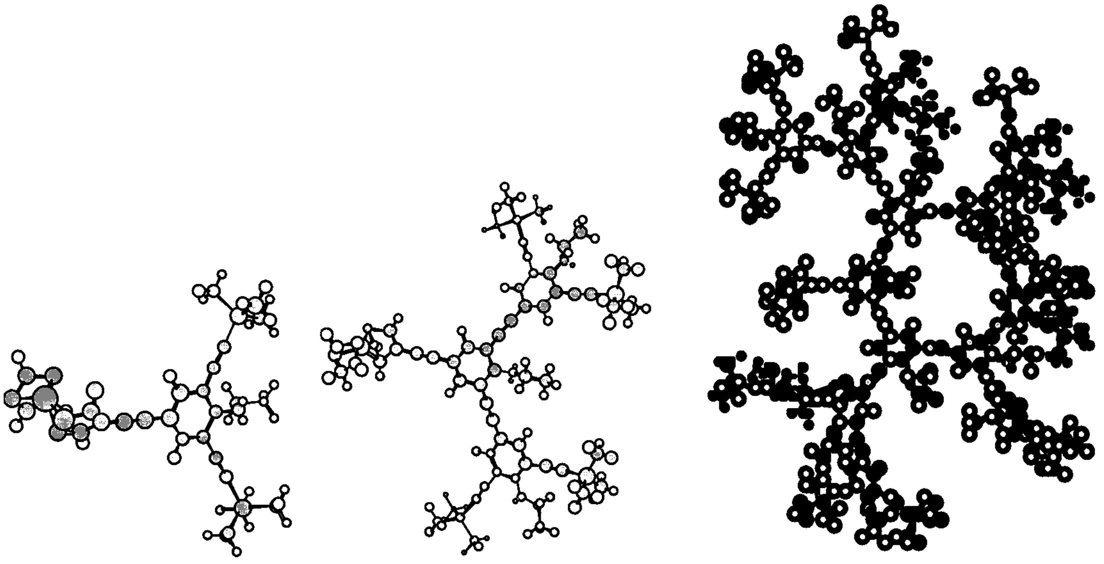
Fc-G1 **Fc-G2** **Fc-G4**

Figure 2. Optimized conformation of **Fc-G1**, **Fc-G2**, and **Fc-G4** by the MM2 force field method.

one portion was replaced with hydrogen atoms by reacting with tetrabutylamine fluoride (TBAF) in THF to give polymer-supported diacetylene **P-G1-(H)$_2$**. The other portion was heated to 115 °C in methane iodide in a sealed tube to give aryl iodide **I-G1-(TMS)$_2$**. A similar Heck–Cassar–Sonogashira–Hagihara reaction of **P-G1-(H)$_2$** and **I-G1-(TMS)$_2$** gave the second-generation polymer-supported monodendron **P-G2-(TMS)$_4$**. This procedure was repeated with a doubling of generation number after an iteration to give the fourth-generation polymer-supported monodendron **P-G4-(TMS)$_{16}$**, which was followed by deprotection of the triazene linkage from the solid support in MeI to give the highly soluble fourth-generation monodendron **I-G4-(TMS)$_{16}$**. The advantages of this approach are that the generation number grows very rapidly, and the purification at each step is very simple. Both the core unit (**P-Gn-(H)$_2$***n*) ($n = 1, 2$) and the branching unit (**I-Gn-(TMS)$_2$***n*) ($n = 1, 2, 4$) grew at the same time during the formation of molecular skeleton, which means both divergent and convergent advantages were taken, whereas the shortcomings existing in both divergent and convergent routes were avoided.

Transmittance FT-IR spectroscopy followed the whole solid-phase synthetic approach. The peaks at 2157 cm^{-1} in **P-G1-(TMS)$_2$**, **P-G2-(TMS)$_4$**, and **P-G4-(TMS)$_{16}$** were characteristics of stretching vibration of carbon–carbon triple bond in trimethylsilyl-protected acetylenes. However, after desilylation, the peak at 3311 cm^{-1} was observed in **P-G1-(H)$_2$** and **P-G2-(H)$_4$**, which was characteristic of stretching vibration of carbon–hydrogen in the terminal acetylene. The identity of **I-G1-(TMS)$_2$** and **I-G2-(TMS)$_4$** was well confirmed by NMR and EI-MS. As for **I-G4-(TMS)$_{16}$**, its molecular weight was confirmed by matrix-assisted laser desorption/ionization mass spectroscopy (MALDT-MS, 3804.4), and four distinguished peaks from 7.808 to 7.558 ppm with area ratios of 1:2:4:8 were observed in its ^1H NMR spectrum, which was quite consistent with the prediction.

Another major advantage of this approach lies in that the resulting monodendrons (**G1**, **G2**, and **G4**) can be easily functionalized at both the core and periphery site by well-developed cross-coupling reactions. We can attach different electroactive or photoactive components at the core and/or the periphery, which will fulfill versatile applications of this kind of monodendron. As a preliminary work, we attached the redox-active ferrocene to the core[13] by a similar Heck–Cassar–Sonogashira–Hagihara reaction (Scheme 2) to form electroactive monodendrons. The resulting electroactive monodendrons **Fc-G1**, **Fc-G2**, and **Fc-G4** were also characterized by NMR, EI/MALDI-MS, and EA.

Electrochemical measurements in dilute solutions of these electroactive monodendrons revealed an interesting molecular structure–property relationship. The diffusion coefficients (D_0) were determined by chronoamperometry using a pulse width of 500 ms and a potential step height of 800 mV centered around $E_{1/2}$. Cotrell's equation was used to calculate the value of D_0, which was 2.327×10^{-6}, 1.636×10^{-6}, and 0.781×10^{-6} cm^2/s for **Fc-G1**, **Fc-G2**, and **Fc-G4,** respectively, indicating an obvious attenuation of D_0 with the increase of generation.

Cyclic voltammetry was used to determine the heterogeneous electron-transfer rate k_0. According to Nicholson's method,[14] the kinetic parameter ψ related to the peak−peak separation was obtained, and the rate constant k_0 was calculated by the following equation:

$$k_0 = \psi[D_0 \pi v(nF/RT)]^{1/2}$$

where v is the scanning rate related to the ψ, n is electron-transfer number, F is the Faraday constant, R is the gas constant, T is the ambient temperature, and D_0 is the diffusion coefficient obtained as above. The k_0 was 7.546×10^{-3}, 3.670×10^{-3}, and 0.857×10^{-3} cm/s for **Fc-G1**, **Fc-G2**, and **Fc-G4,** respectively, also revealing an obvious attenuation phenomenon with the increase of generation. This phenomenon agrees with observations previously reported by several groups working with dendrimers containing electroactive cores.[13c,d]

The cyclic voltammograms at different scanning rates are shown in Figure 1. At a sweep rate of 20 mV/s, the peak−peak separation (ΔE_p) for **Fc-G4** (99 mV) is larger than that of **Fc-G2** (90 mV) and much larger than that of **Fc-G1** (70 mV), indicating that the electron transfer between the redox ferrocene and electrode slowed with the increase of the generation. Moreover, when the scanning rates increased from 20 to 500 mV/s, the ΔE_p increased more dramatically for **Fc-G4** than that for **Fc-G1** and **Fc-G2**, indicating a quasi-reversible electrochemical process for **Fc-G1** and **Fc-G2** while an irreversible one for **Fc-G4**. This relationship between the molecular structure and electron-transfer rate attenuation can be rationalized by the environmental change of redox ferrocene component. Computational conformation of monodendrons **Fc-G1**, **Fc-G2**, and **Fc-G4** indicated that the redox couple was encapsulated more seriously with the increase of generation (Figure 2), and this encapsulation strongly affected the electron-transfer rate between the redox couple and the electrode.

In conclusion, an efficient solid-supported iterative divergent/convergent synthetic strategy was developed to prepare soluble phenylacetylene monodendrons. Attachment of redox ferrocene at the core revealed an obvious electron-transfer attenuation with increasing generation due to the increase of steric capsulation of redox couple. Further functionalization on these monodendrons and study on the intramolecular electron/energy transport process are under way in our group.

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Supporting Information Available: Details of the synthesis of all compounds, details of spectrometry analysis, and details of chronoamperometry experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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