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Tetraphenylmethane-based tectons in dendrimer synthesis: convergent assembly of ferrocene dendrimers

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Abstract—A ferrocene dendrimer having nine electrochemically equivalent surface ferrocene units was constructed from a new tetraphenylmethane-based triferrocenyl dendron via a facile convergent approach.

The synthesis of peripherally functionalized redox-active dendrimers has been the focus of many recent studies.[1,2] Since ferrocenes show stable redox properties and are easy to functionalize,[3] ferrocene dendrimers are a widely studied class of redox-active dendrimers.[4] Until now, most of the ferrocene dendrimers have been prepared via the divergent approach where multiple ferrocene residues were coupled to the surface of a preformed dendrimer in the final synthetic step. However, divergent strategies may lead to incomplete couplings, especially at higher generations, resulting in constitutional defects. This, in turn, may severely affect the overall electrochemical properties of the dendrimers. To circumvent these problems, convergent synthetic routes[5] to ferrocenyl dendrimers, albeit a few, have recently appeared in the literature.[6] Prompted by these reports, we now present here the use of a new triferrocenyl dendron based on a tetraphenylmethane scaffold for the convergent assembly of a nonaferrocenyl dendrimer via iterative use of multifold Pd-catalyzed reactions.

We have recently described a topologically new AB_3 tecton **2** (readily derived from New Fuchsin **1**) based on a tetraphenylmethane scaffold.[7] We now report its use in the convergent synthesis of ferrocenyl dendrimers.[8] Thus, a three-fold Heck reaction of **2** with vinyl ferrocene under Jefferey's conditions ($Pd(OAc)_2$, Bu_4NBr, KOAc, DMF, 80°C)[9] gave rise to the triferrocenyl phenol **3** in 70% yield after purification by preparative thin layer chromatography (silica gel, 10% EtOAc in light petroleum) (Scheme 1).[10] It was expected that **3**, due to its disrupted conjugation at the central carbon atom, would allow no communication whatsoever between its attached ferrocene rings and hence provide three electrochemically equivalent ferrocene units. Cyclic voltammetric studies on **3** (CH_3CN, Pt anode, Bu_4NClO_4, 25°C) produced a single reversible redox wave ($E_{1/2}=+0.32$ V versus SCE, $\Delta E_p=70$ mV) indicating that the three ferrocene units in **3** are indeed electrochemically equivalent. The phenol **3** was next converted to the propargyl ether dendron **4** (propargyl bromide, aq. NaOH, CH_2Cl_2, rt) in 80% yield and the latter coupled with 1,3,5-tribromobenzene (**5**) under Sonogashira-coupling conditions *without using CuI* ($Pd(dba)_2$, $4PPh_3$, DMF, Et_3N, 70°C) to give the nonaferrocenyl dendrimer **6** (36%) after purification by silica gel column chromatography (light petroleum:$CHCl_3$:EtOAc 5:4:1). The coupling reaction between **4** and **5** must be carried out *in the absence of CuI* (a co-catalyst routinely used for Sonogashira couplings) which otherwise led to extensive copper-induced dimerization of **4**. The dendrimer **6** was characterized by its ^1H and ^{13}C NMR spectra.[10] The ^{13}C NMR spectrum of **6** was particularly diagnostic and, in addition to peaks due to the propargyl ether dendron **4**, showed resonances at δ 123.1 and 134.9 due to the central benzene core. The MALDI-TOF mass spectrum of **6** showed a dominant M+1 peak at m/z 3212.29 (calcd for $C_{207}H_{174}Fe_9O_3$: 3211.05). Cyclic voltammetric studies on **6** (CH_2Cl_2, Pt anode, Et_4NClO_4, 25°C) produced a single redox wave ($E_{1/2}=-0.18$ V versus Fc/Fc^+) indicating that all the nine ferrocene units in this dendrimer are electrochemically equivalent. However, for reasons not clear to us at this moment, the redox

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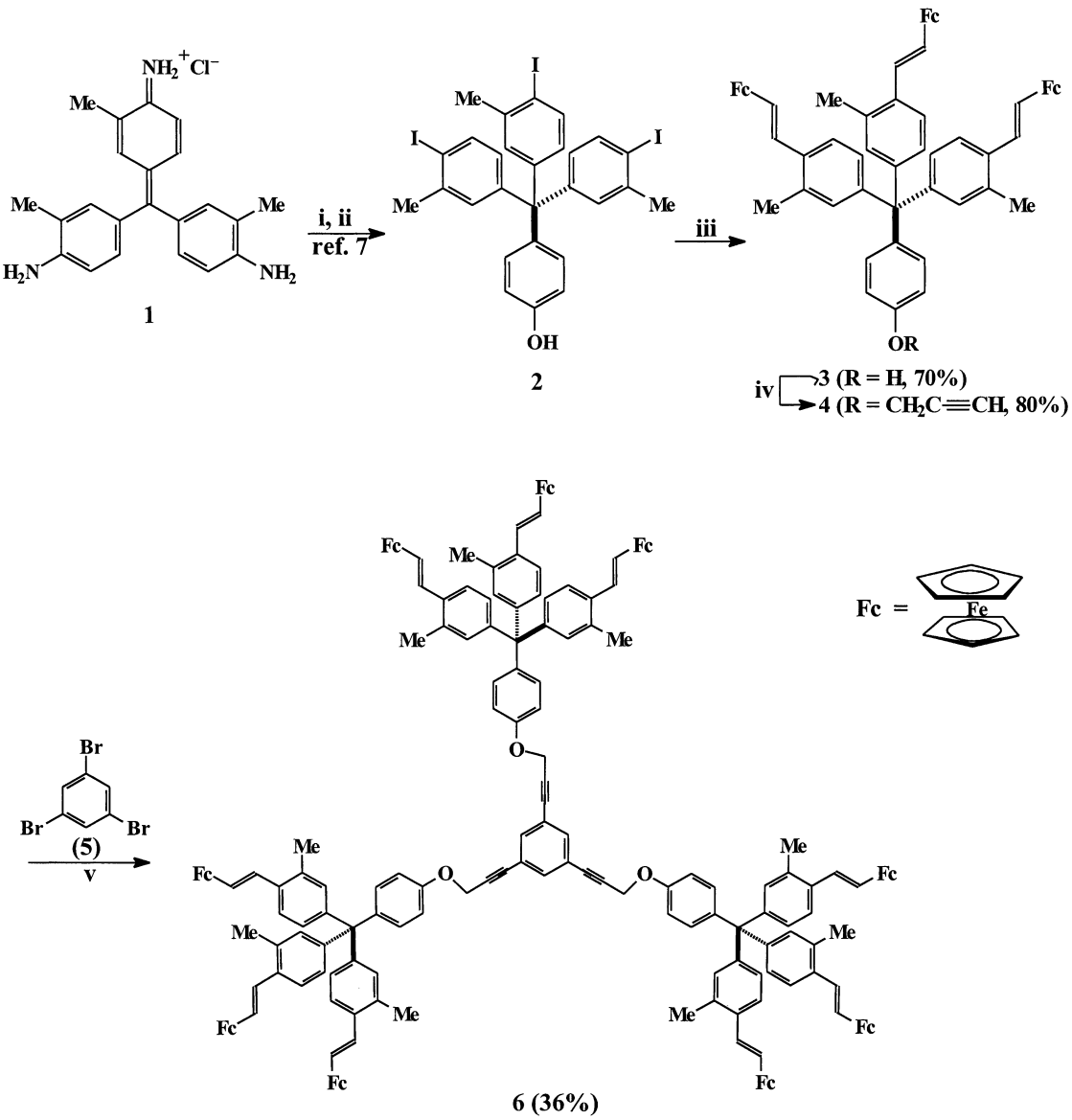

Scheme 1. (i) $NaNO_2$, dil. HCl, 0°C, then KI, rt; (ii) phenol, cat. conc. H_2SO_4; (iii) vinyl ferrocene, 30% $Pd(OAc)_2$, Bu_4NBr, KOAc, DMF, 80°C, 30 h; (iv) propargyl bromide, 50% aq. NaOH, CH_2Cl_2, rt, 24 h; (v) 30% $Pd(dba)_2$–$4PPh_3$, DMF, Et_3N, 70°C, 30 h.

wave gradually flattened on repeated scans, even at fast scan rates (400 mV/s). Perhaps, the oxidized form of the dendrimer was not chemically stable under these conditions.

In summary, we have described a new triferrocenyl dendron with a central branching point which provides three non-communicative ferrocene units at its periphery. Its utility in the convergent synthesis of a nonaferrocenyl dendrimer using a three-fold Sonogashira reaction has been demonstrated.

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10. All new compounds gave satisfactory spectral data. Compound **3**: mp 161–162°C ($CHCl_3$/MeOH); IR (KBr, cm^{-1}): 2920, 1630, 1500, 1170, 1100; ^1H NMR (300 MHz, $CDCl_3$): δ 2.30 (s, 9 H), 4.13 (s, 15 H), 4.27 (s, 6 H), 4.45 (s, 6 H), 6.73 (d, $J=8.7$ Hz, 2 H), 6.74 (d, $J=16$ Hz, 3 H), 6.88 (d, $J=16$ Hz, 3 H), 7.03–7.12 (m, 6 H), 7.15 (d, $J=8.6$ Hz, 3 H), 7.42 (d, $J=8.7$ Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.3, 63.7, 66.8, 68.9, 69.2, 83.9, 114.2, 123.5, 123.9, 127.7, 129.0, 132.2, 132.7, 133.7, 134.1, 139.4, 145.6, 153.3. Anal. calcd for $C_{64}H_{56}Fe_3O$: C, 76.24; H, 5.55. Found: C, 76.51; H, 5.36. Compound **6**: mp >250°C; ^1H NMR (300 MHz, $CDCl_3$): δ 2.29 (s, 27 H), 4.12 (s, 45 H), 4.25 (s, 18 H), 4.44 (s, 18 H), 4.83 (s, 6 H), 6.74 (d, $J=8.3$ Hz, 9 H), 6.81–6.95 (m, 15 H), 6.96–7.11 (m, 18 H), 7.21 (d, $J=8.2$ Hz, 6 H), 7.42 (d, $J=8.3$ Hz, 9 H), 7.47 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.3, 63.7, 66.8, 68.9, 69.5, 83.9, 85.1, 85.6, 113.8, 123.1, 123.6, 123.9, 127.7, 129.1, 132.1, 132.7, 133.7, 134.2, 134.9, 140.1, 145.5, 155.7; MS (MALDI-TOF): m/z 3212.29 (M+1), calcd for $C_{207}H_{174}Fe_9O_3$: 3211.05.