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LETTERS

Synthetic studies on tetraphenylmethane dendrimers

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Abstract

A convergent synthesis of a first generation centrally tetrahedral phenyl cinnamate dendrimer and related dendrons using a multifold Heck reaction strategy is described. © 1999 Published by Elsevier Science Ltd. All rights reserved.

There is a considerable current interest in the synthesis of centrally tetrahedral molecular architectures due to their potential applications in different spheres of material science.[1–5] Such molecules, for example, can be used as moleculer caltrops in scanning probe microscopy as shown with nanometric tripodaphyrins based on a tetraphenyl methane (TPM) core[1a,b] or as new molecular electronic devices, as demonstrated with TPM based spiro-fused conjugated oligomers.[2] Tetraphenyl methane based cobalt clusters containing up to 40 cobalt atoms have recently been prepared in the search of new materials.[3] It has also been shown that moleculer morphology can be precisely controlled with centrally tetrahedral conjugated hydrocarbons, especially with tetra-stilbenoid methane derivatives.[4] On the other hand, a number of tetraphenylmethane derivatives, owing to their rigid tetrahedral framework which precludes intramoleculer interactions between their chromophores, have given rise to supramoleculer assemblies through intermoleculer non-covalent interactions.[6] We envisaged that dendritic architectures comprised of centrally tetrahedral repeating units may also lead to interesting morphology and physicochemical properties and initiated a program on the synthesis of some centrally tetrahedral dendrimers **1a–c** based on a tetraphenylmethane (TPM) core. Although, in recent years, great strides have been made towards synthesis of various types of dendrimers,[7] there are no reports on genuine dendrimers that are based on a fully substituted centrally tetrahedral core. In this communication, we now report our preliminary results on the synthesis of a first generation TPM-based phenyl cinnamate dendrimer **1a.G$_1$** and in addition, present a facile synthetic approach towards TPM-based dendrons for utilization in higher generation dendrimer synthesis.

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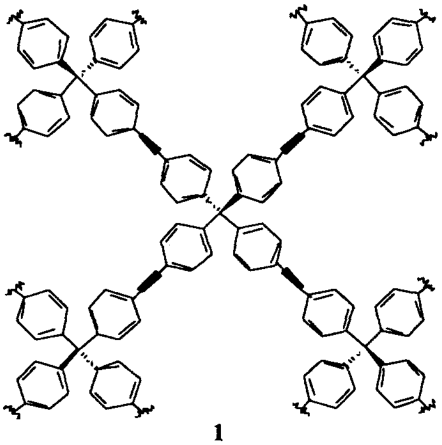

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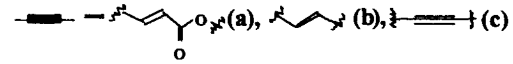
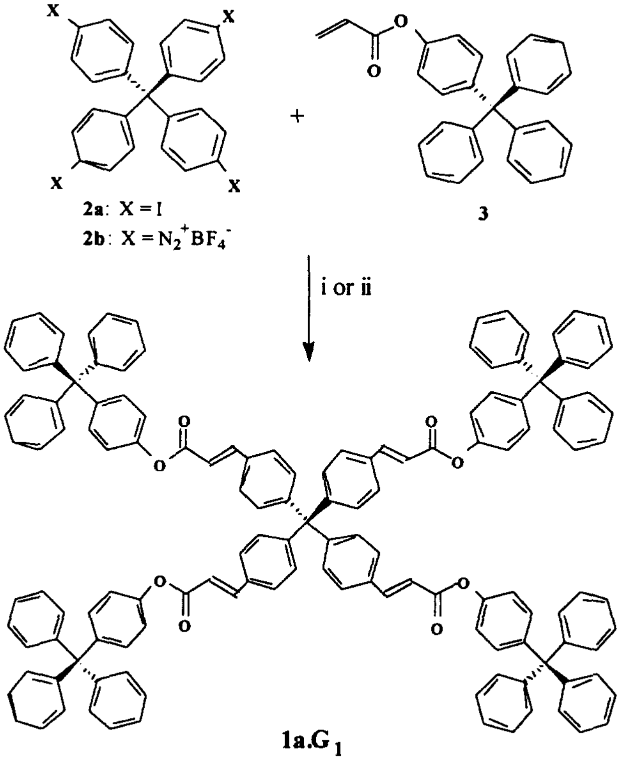
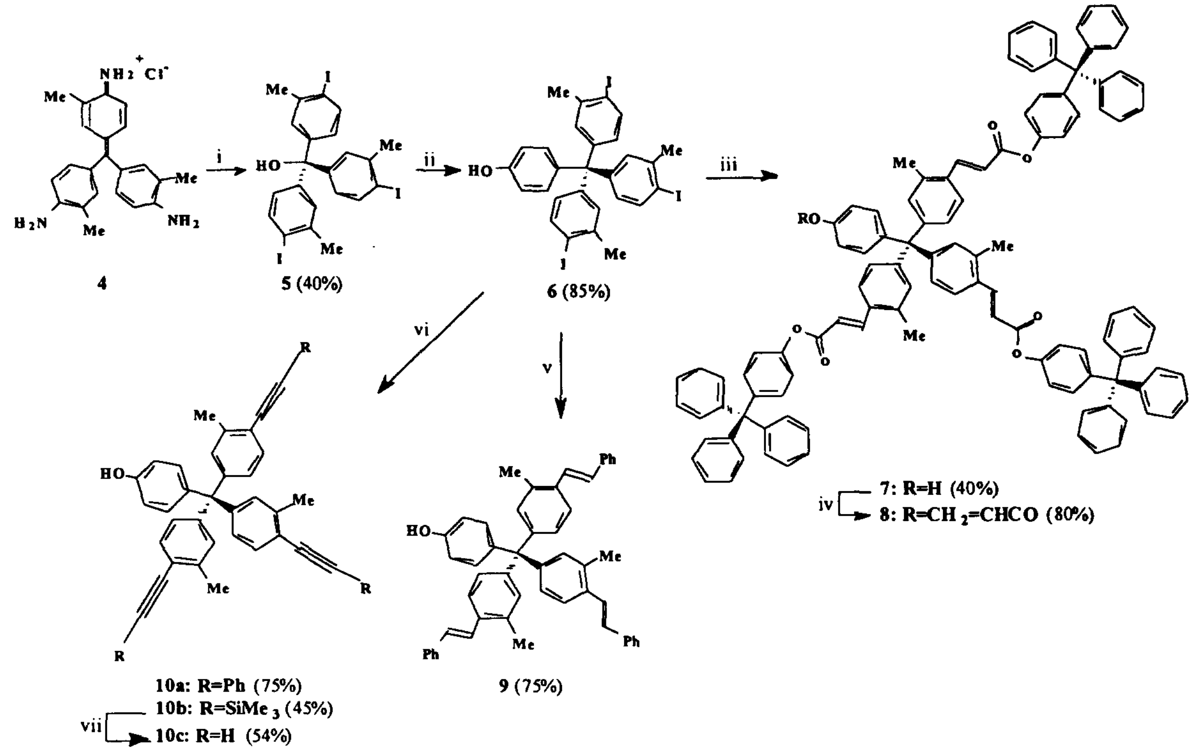


The TPM-based cinnamate dendrimer **1a.G$_1$** was synthesized in a convergent approach via a fourfold Heck reaction of tetra(*p*-iodophenyl)methane (**2a**)[5c] with the *p*-tritylphenyl acrylate wedge **3** (4.5 equiv.), the latter being readily prepared from *p*-trityl phenol and acryloyl chloride (Scheme 1). The best results were obtained under Jeffery's phase transfer conditions ($Pd(OAc)_2$, Bu_4NCl, $NaHCO_3$, DMF, 80°C)[8] which gave **1a.G$_1$** in 50% yield after column chromatography over silica gel (5–20% EtOAc in pet. ether)



Scheme 1. (i) **2a**, **3** (4.5 equiv.), 30% $Pd(OAc)_2$, Bu_4NCl, $NaHCO_3$, DMF, 80°C (50%); (ii) **2b**, **3** (4 equiv.), 20% $Pd(OAc)_2$, EtOH, 80°C (20%)



Scheme 2. (i) $NaNO_2$, H_2SO_4, 0°C then KI, H_2O, 80°C; (ii) conc. H_2SO_4, phenol; (iii) **3** (4 equiv.), 30% $Pd(OAc)_2$, Bu_4NCl, $NaHCO_3$, DMF, 80°C; (iv) $CH_2{=}CHCOCl$, Et_3N, CH_2Cl_2; (v) styrene (5 equiv.), 25% $Pd(OAc)_2$, Bu_4NCl, K_2CO_3, DMF, 80°C; (vi) RC≡CH (5 equiv.), 25% $PdCl_2(PPh_3)_2$, Et_3N, CuI, DMF, rt; (vii) K_2CO_3, MeOH, rt

(R_f 0.4, 15% EtOAc in pet. ether).[9] Poor conversions (<10%) were obtained under traditional Heck reaction conditions ($Pd(OAc)_2$, Et_3N with or without added $P(o\text{-}Tol)_3$) even after prolonged reactions. In view of the superior Heck-reactivity of arenediazonium salts over iodoarenes,[10] the fourfold Heck reaction of the octazonium salt **2b**[5d] with **3** (4.5 equiv.) was also studied (20% $Pd(OAc)_2$, EtOH, 80°C)[5d] which, however, gave only poor yields of **1a.G$_1$** (20%; 42% based on recovered **3**), presumably due to the limited solubilities of both the starting materials and the product in EtOH. Compound **1a.G$_1$** was fully characterized by its ^1H and ^{13}C NMR spectra. Further confirmation of its structure came from its FAB-MS data which showed the $M^+{-}1$ ion at *m/z* 1871.[9]

We next turned our attention towards synthesis of phenyl cinnamate dendrons for use in the convergent assembly of higher generation cinnamate dendrimers **1a**. For this, our primary goal was to synthesize an appropriate TPM-based AB_3 tecton. Towards this goal, New Fuchsin (**4**) was converted via conventional hexazotization and a threefold Sandmeyer reaction to the tri(iodoaryl)carbinol **5** in 40% overall yield (Scheme 2). Friedel–Crafts reaction of phenol with **5**, under H_2SO_4 catalysis, then gave the *p*-(tri-iodotrityl)phenol derivative **6** (85%),[9] our desired AB_3 tecton. A threefold Heck reaction of **6** with the acrylate wedge **3** (3.5 equiv.), again under Jeffery's phase transfer conditions, produced the key phenol **7** (42%)[9] after silica gel chromatography (5–25% EtOAc in pet. ether) (R_f 0.3, 20% EtOAc in pet. Ether) and the latter upon acylation with acryloyl chloride then gave the second generation phenyl cinnamate dendron **8** in 80% yield.

The AB_3 tecton **6** also appeared to be ideally suited for the synthesis of other TPM-based dendrons that may be used towards convergent assembly of the conjugated dendrimers **1b,c**. Thus, it was envisaged that threefold Pd-catalyzed couplings of **6** with TPM-based styryl or acetylenic wedges, conversion of the resultant phenol to a triflate followed by fourfold coupling of the latter with tetra(*p*-styryl)methane[5c] or tetra(*p*-ethynylphenyl) methane[1b] would lead to the dendrimers **1b,c**. Moreover, such tripodal triflates appeared to be potentially useful in the synthesis of carbon-centered moleculer caltrops.[1c] In view of such promises, we carried out some model studies on threefold Pd-catalyzed couplings of **6**. Thus, a threefold Heck reaction of **6** with styrene gave rise to the tristilbenoid dendron **9** in 75% yield whereas Sonogashira-couplings of **6** with phenylacetylene and trimethylsilyl-acetylene led to the linear conjugated TPM dendrons **10a,b** in somewhat moderate yields (Scheme 2). The tris-trimethysilylethynyl adduct **10b** was subsequently desilylated with K_2CO_3 in MeOH to give the highly useful AB_3 tecton **10c** in 54% yield.

In summary, we have synthesized the first generation of a centrally tetrahedral phenyl cinnamate dendrimer using a fourfold Heck reaction strategy. A short synthetic sequence leading to higher generation TPM-based cinnamate, stilbene and tolan dendrons have also been developed starting from a cheap dyestuff material. Convergent assembly of these dendrons with appropriate central cores towards synthesis of higher generation TPM dendrimers **1a–c** is currently under investigation.

Acknowledgements

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9. Compound **1a.G$_1$**: FAB-MS: *m/z* 1871 (M^+–1); ^{1}H NMR (300 MHz, $CDCl_3$): 6.59 (d, 4H, J=16 Hz), 7.06 (d, 8H, J=8.8 Hz), 7.16–7.31 (76H, m), 7.48–7.53 (8H, m), 7.82 (d, 4H, J=16 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): 64.7, 68.2, 117.9, 120.3, 126.0, 127.5, 127.9, 131.1, 131.3, 132.1, 132.6, 144.3, 145.5, 146.6, 148.1, 148.8, 165.1. Compound **6**: ^{1}H NMR (300 MHz, $CDCl_3$): 2.33 (s, 9H), 6.65 (dd, 3H, J=8.4, 2.4 Hz), 6.70 (d, 2H, J=6.6 Hz), 6.99 (d, 2H, J=6.6 Hz), 7.02 (d, 3H, J=2.1 Hz), 7.65 (d, 3H, J=8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): 28.2, 63.3, 98.7, 114.5, 130.1, 131.9, 137.8, 138.0, 140.5, 146.5, 153.6. Compound **7**: ^{1}H NMR (500 MHz, $CDCl_3$): 2.44 (s, 9H), 6.58 (d, 3H, J=15.8 Hz), 6.81 (d, 2H, J=8.7 Hz), 7.11–7.33 (65H, m), 7.59 (d, 3H, J=8.5 Hz), 8.16 (d, 3H, J=15.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): 20.2, 64.1, 64.6,

114.6, 118.1, 120.3, 126.0, 127.5, 129.1, 131.1, 132.1, 133.0, 137.3, 143.6, 144.2, 146.6, 148.7, 153.9, 165.4. Compound **9**: ^{1}H NMR (300 MHz, $CDCl_3$): 2.35 (s, 9H), 6.73 (d, 2H, J=8.7 Hz), 7.00 (d, 3H, J=16.2 Hz), 7.05–7.11 (m, 6H), 7.14 (d, 2H, J=8.7 Hz), 7.20–7.31 (m, 6H), 7.34 (d, 3H, J=5.4 Hz), 7.35 (d, 3H, J=15 Hz), 7.45–7.54 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): 20.2, 63.7, 114.3, 124.4, 126.1, 126.5, 127.4, 128.6, 129.1, 129.7, 132.2, 132.7, 133.7, 134.7, 137.8, 139.2, 146.3, 153.4. Compound **10c**: ^{1}H NMR (300 MHz, $CDCl_3$): 2.35 (s, 9H), 3.26 (s, 3H), 6.70 (d, 2H, J=8.7 Hz), 6.93 (d, 3H, J=8.0 Hz), 7.00 (d, 2H, J=8.5 Hz), 7.01 (s, 3H), 7.33 (d, 3H, J=8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): 20.9, 64.0, 80.9, 82.3, 114.5, 119.6, 128.3, 131.7, 132.1, 138.0, 139.9, 147.0, 153.7.

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