Rapid Communication

Synthetic studies on tetrastilbenylmethane dendrimers: preparation and optical properties of a second generation dendron

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Received 28 August 2002; accepted 30 January 2003

Towards synthesis of tetrastilbenylmethane dendrimers, a second generation tristilbenylmethylstyrene dendron has been prepared from the commercial dye stuff New Fuchsin. Heck reaction of arenediazonium salts with vinyl trimethylsilane is strategically used to construct the focal styrene unit of the dendron. Preliminary optical studies show strong absorption and emission properties for this dendron.

Because of its interesting topological features, tetrastilbenylmethane has attracted much current attention as a pluripotential building block. In tetrastilbenylmethane and its derivatives, the central carbon atom orients its substituents in a rigid tetrahedral array so that there is little or no scope of any intramolecular interactions. In an elegant study, Bazan \textit{et al.} have shown that if the substituents are sufficiently large, they even prevent intermolecular associations resulting in a stable amorphous phase\textsuperscript{1}. The central carbon of tetrastilbenylmethane also causes a disruption in conjugation between its substituents so that the latter behave as electronically independent entities. These features have been exploited to construct a number of molecular architectures with potential applications in materials and biological sciences\textsuperscript{15}. Important examples are three dimensional metallostars\textsuperscript{2}, amorphous molecular glasses including those having hole transporting properties\textsuperscript{3}, electrogendrated conducting polymers\textsuperscript{4}, supramolecular host assemblies\textsuperscript{5}, light harvesting modules\textsuperscript{6}, star shaped chromophoric and/or electroactive modules\textsuperscript{7}, three dimensional functional nanoparticles\textsuperscript{8}, etc. We have recently reported the synthesis of a number of dendritic architectures based on tetrastilbenylmethane. These include redox active multifunctional dendrimers\textsuperscript{9} and a centrally tetrahedral carbohydrate cluster\textsuperscript{10}. In continuation of these studies and in view of the current focus on stilbenoid macro-molecules e.g. poly(p-phenylenevinylene)s (PPVs) and its oligomers for applications in light emitting diodes (LEDs)\textsuperscript{11}, we became interested in the synthesis of tetrastilbenylmethane dendrimers viz. A. Linear polymers such as PPVs are crystalline in nature and hence suffer from strong intermolecular associations in the solid phase. This ultimately lead to excimer formations resulting in diminished fluorescence efficiencies. We envisaged that the dendrimer A, due to its three dimensional structure would be free from intermolecular associations and moreover, due to its rigid and large molecular volume, would show a stable (amorphous) solid state morphology. These features promised a superior emission efficiency for the dendrimer.

The synthesis of A was planned via a convergent approach through four fold Heck reaction of the tristilbenylmethyl styrene dendron 1 with the known tetra(piodophenyl)methane (2)\textsuperscript{12} as shown in \textbf{Scheme I}. In this communication, our preliminary results on the synthesis of a second generation tristilbenylmethyl styrene dendron in a few steps from the cheap dye stuff New Fuchsin are described. Heck reaction of arenediazonium salts with vinyl trimethylsilane has been used as the key reaction to construct the focal styrene unit of the dendron.

The feasibility of styrene synthesis via the diazoniumvinyl silane Heck protocol\textsuperscript{13} was first tested with p-trityl aniline 3, as a model (\textbf{Scheme I}). Thus, 3 was converted to its diazonium tetrafluoroborate 4 (NaNO\textsubscript{2}, HOAc, conc. H\textsubscript{2}SO\textsubscript{4}, 0 °C thenaq. NaBF\textsubscript{4}) and the latter subjected to Heck reaction with vinyl trimethylsilane using Pd(dba\textsubscript{3}) as the catalyst (CH\textsubscript{2}CN, rt)\textsuperscript{14}. This led to a fast reaction (over in 30 min) resulting in a mixture of the styrly silane 5a and the desired styrene 5b in good yield. This mixture of styrenes (5a and 5b) could be quantitatively converted to the desired styrene 5b via an acid catalyzed protodesilylation reaction (cone. HCl, THF, reflux, 30 min) resulting in a 40% overall yield of 5b from 3\textsuperscript{15}. The Heck reaction between the diazonium salt 4 and vinyl trimethylsilane deserves several comments. The amount of vinyl trimethylsilane and the order of addition of the reagents were found to be critical for the success of this reaction. Using one equivalent or a slight excess of vinyl silane led to considerable...
amounts of the corresponding stilbene via a second Heck reaction of unreacted arenediazonium salts with the product styrenes. Best yields were obtained using eight to ten equivalents of vinyl trimethylsilane and by adding the diazonium salt last to a solution of the vinyl silane and the catalyst in CH$_2$CN at room temperature. Raising the reaction temperature or addition of any base or phosphine ligands had a detrimental effect on this reaction due to rapid decomposition of the diazonium salt. Pd(dba)$_2$ was the catalyst of choice since Pd(OAc)$_2$ in CH$_2$CN or MeOH did not lead to the desired products although nitrogen evolution was observed in both cases. Vinyl triethoxysilane, a cheaper variety of vinyl silane, was also examined as the olefinic component which, however, produced a complex product mixture from which 5a,b were isolated in poor yields.

Having found the conditions for aniline to styrene conversion, we then set out to prepare a tristilbenylmethyl aniline to be converted to the tristilbenylmethyl styrene dendron viz. 1. Since Estilbenoid linkages were deemed essential for high fluorescence yields of the dendrimer A, Heck arylation of styrenes, which is known to produce Estilbenes with high stereoselectivity, was used to construct the tristilbenoid wedge of our dendron. In the event, we started with the cheap commercially available dyestuff New Fuchsin 6 which via three fold diazotization (NaNO$_2$, conc. H$_2$SO$_4$, 0 °C and Sandmeyer reaction with KI) produced the triiodoaryl carbinol 7 in 40% overall yield (Scheme III). Three fold Heck reaction of 7 with styrene under Jeffery's phase transfer conditions (Pd(OAc)$_2$, Bu$_4$NBr, K$_2$CO$_3$, DMF, 80°C) then produced the tristilbenyl methyl alcohol 8 in 66% yield after chromatographic purification over silica gel. The $^1$H NMR (300 MHz) spectrum of 8 showed a large coupling constant (J = 16 Hz) for the stilbenyl olefinic protons indicating a
An acid catalyzed Friedel-Crafts reaction of 8 with aniline (aniline hydrochloride, HOAc, 100°C) then led to the p(tristilbenylmethyl)aniline derivative 9 in 64% yield. An alternate approach to 9 via prior acid catalyzed alkylation of aniline with 7 followed by three fold Heck reaction with styrene was also investigated but was discarded due to poor yields. The amino group in 9 was then diazotized to the corresponding diazonium tetrafluoroborate (NaNO₂, conc. HCl, 0°C then aq. NaBF₄) and the latter subjected to Heck reaction with excess vinyl trimethylsilane (Pd(dbu)₂, CH₂CN, rt) which again led to a fast reaction (complete within 30 min) producing a mixture of the styril silane 10a and the desired tristilbenylmethyl styrene 10b. Brief exposure of this mixture to aqueous acid (conc. HCl, THF, reflux, 30 min) led to smooth protodesilylation of 10a (to 10b) resulting in a 30% overall yield of 10b from 9.

In order to get a preliminary idea about the optical
properties of the dendrimer A, steady state optical studies were carried out with 10b. The latter showed an intense absorption band at 316 nm (10^5 M in CH2Cl2, ε = 1.0 x 10^5 M^-1 cm^-1). The absorption maximum is 21 nm red shifted from that of stilbene, pointing to some delocalization between the stilbene units through the central tetrahedral carbon (homocoujugation). Similar observations have also been made by Bazan et al. for tetristilbenylmethane 1a,b. Interestingly, although 10b has three stilbene units in a nonconjugated fashion, its molar absorptivity is much greater than three times the value of stilbene (25,000 M^-1 cm^-1) indicating a strong excitation splitting 7b,c,20 between the stilbene arms in 10b i.e. the excitation in 10b is not limited to any one stilbene unit but is spread over all three stilbene arms. 10b also produced a strong fluorescence with a maximum at 387 nm (λexc = 316 nm) which is also red shifted from that of stilbene by 25 nm. The emission spectrum did not show any extended red tailing which suggests that intermolecular association (excimer formation) is not significant in this case. This was as predicted by our design principle (vide supra) since intermolecular stacking in 10b is strongly disfavoured by the rigid centrally tetrahedral nature of the molecule. These features promise that the proposed dendrimer A should have a strong emission property.

In conclusion, we have described a short synthetic sequence to a second generation tristilbenylmethyl styrene dendron 10b starting from readily available starting materials. Four-fold Heck coupling of 10b with the tetraiodo core 2 towards synthesis of the terristilbenylmethane dendrimer is currently under way.

Acknowledgement
One of us (SKS) thanks CSIR, New Delhi for a senior research fellowship.

References
15. Sc: mp 184-185°C (CHCl3-MeOH); 'H NMR (CDCl3, 300 MHz): δ 5.22 (d, J = 11 Hz, 1H), 6.09 (dd, J = 11, 18 Hz, 1H), 7.157,31 (m, 19H).
18 $^1$H NMR (CDCl$_3$, 300 MHz) 7: $\delta$ 2.40 (s, 9H), 6.72 (dd, $J = 8.4$, 2.1 Hz, 3H), 7.18 (d, $J = 2.1$ Hz, 3H), 7.74 (d, $J = 8.4$ Hz, 3H). 8: $\delta$ 2.38 (s, 9H), 2.76 (t, 1H), 6.99 (d, $J = 16.1$ Hz, 3H), 7.11 (d, $J = 7.8$ Hz, 3H), 7.19 (s, 3H). 7.237.36 (m, 12H), 7.477.52 (m, 9H). 9: $\delta$ 2.35 (s, 9H), 3.64 (t, 3H), 6.59 (d, $J = 8.7$ Hz, 2H), 6.99 (d, $J = 16.2$ Hz, 3H). 7.04 (d, $J = 8.7$ Hz, 2H), 7.077.15 (m, 6H), 7.227.28 (m, 6H), 7.30 (d, $J = 16.2$ Hz, 3H), 7.35 (t, $J = 7.2$ Hz, 3H), 7.36 (d, $J = 7.2$ Hz, 3H), 7.477.52 (m, 6H). 10b: $\delta$ 2.35 (s, 9H), 5.23 (d, $J = 11$ Hz, 1H), 5.73 (d, $J = 17.4$ Hz, 1H), 6.70 (dd, $J = 11$, 17.4 Hz, 1H), 7.00 (d, $J = 16.2$ Hz, 3H), 7.057.11 (m, 6H), 7.227.28 (m, 9H), 7.307.38 (m, 10H), 7.50 (d, $J = 7$ Hz, 6H).
