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This report describes our progress in the development of STARBURST dendrimers for use as multiperformance materials. Specifically we are preparing conjugated dendritic structures based on the stilbene moiety. Progress in this area looks very promising.

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DEVELOPMENT OF MULTIPERFORMANCE MATERIALS

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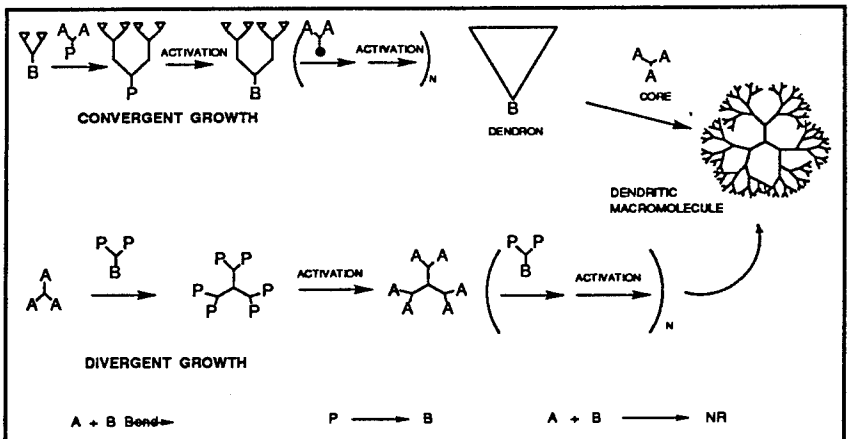
Introduction

Ever since the pioneering work of Tomalia and coworkers at Dow Chemical Company,[1] the field of dendritic macromolecules has caught the attention of a large community of scientists ranging from chemists[2] to physicists[3] and even more recently molecular biologists[4] have caught the excitement of these unique polymers. Both the molecular architecture and the synthetic control of the dendrimer structure are the key components that have helped to catalyze the excitement in these diverse areas. Dendrimers are highly branched molecules which retain high solubilities, contain a large number of reactive chain end groups, and very high level of precision is maintained in the polymer structure due to the their stepwise method of construction. A wide variety of polymer repeat units have been used in the synthesis of dendrimers including organic[5] and even organometallic[6] repeat units.

Poly(amidoamine) dendrimers (PAMAM) were the first family of dendritic macromolecules that were prepared with high molecular weights, and extensively characterized by a variety of analytical techniques including NMR, ESR, ES-MS, SEC, and capillary electrophoresis.[7] The synthesis of PAMAM dendrimers is amendable to scaling up size the size of the reactions so that for the first time it is possible to make larger quantities of these materials. Having large quantities of dendrimer allows for investigation of many of the physical properties of dendrimers such as rheological. By comparing the important physical properties of dendrimer to those of traditional polymer architectures, such as linear, branched and crosslinked, allows for a greater understanding of how the unique properties of this architecture influence their physical properties.

Dendritic macromolecules have been grown by either by a divergent or via a convergent route. Scheme 1 shows the differences between these two strategies. The divergent approach starts from a core molecule and the structure is built in a

radial fashion outward from the core. In contrast, convergent growth starts with the chain ends of the dendrimer to which monomer units are added to form a dendron which is then hooked onto a core molecule. Each of these methods has its advantages and disadvantages. The convergent approach allows for careful control of the surface group functionality, for example, it is the only approach by with a differentiated dendrimer, that is different functional groups at precisely located places on the surface of the dendrimer, have been made.[8] The difficulty with this method is as higher molecular weight dendrons are prepared it becomes more and more difficult to hook the dendrons onto a core molecule. In contrast, it is possible to prepare very high molecular weight dendrimers, molecular weights over 1 x 10^6 have been prepared, by the divergent method, and also it is the only method currently being used to commercialize dendritic macromolecules.



Scheme 1

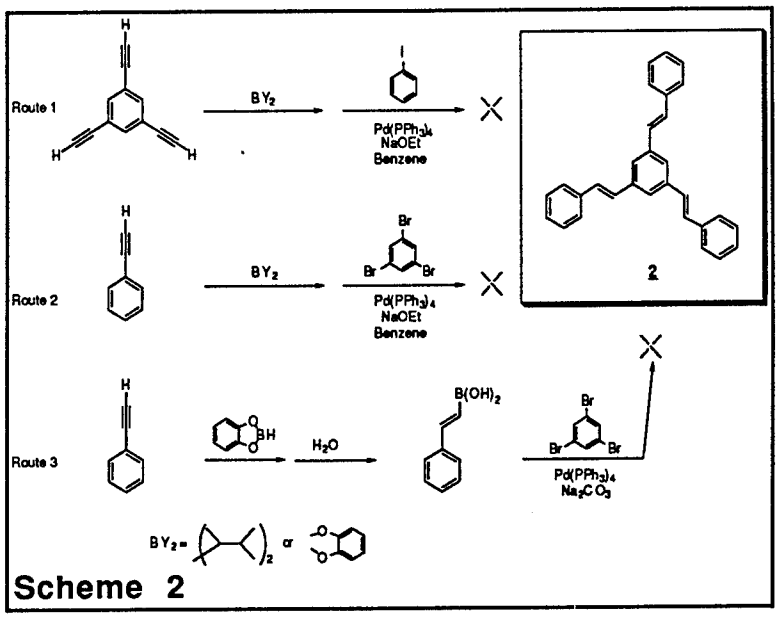
While much of our work at MMI has concentrated on the preparation and modification of PAMAM dendrimers, this report will cover our progress in the synthesis of a unique class of dendrimers based on stilbene moieties.

Stilbene-based Dendrimers

Our goal for this project was to see polymers with unique optical and electronic properties could be prepared through the synthesis of dendrimers comprised of

stilbene linkages. Our work builds on the success that Jeffrey Moore and his group have had in extensively exploring the chemistry of dendritic macromolecules prepared from phenylacetylene repeat units.[9] Our synthetic approach is to use the efficient palladium-catalyzed cross coupling reaction between an arene ring and a vinyl moiety to build up the dendritic structure.

Figure 1 shows computer generated models for a series of highly branched stilbene-based branched molecules and dendrimers. At low generations the molecules are fairly planer with a slight twist around the stilbene linkage, but higher generations were found to adopt a more bowl-like shape. Also the rigidity of these structures indicates one of the difficulties in preparing this class of molecules will be their poor solubility, a characteristic which is shared by linear poly(phenylene vinylene) polymers. The poor solubility of these materials was indeed one of the chief experimental difficulties that we encountered in their preparation.



Scheme 2

Divergent Growth

A model study was undertaken to see if the divergent growth of these molecules was feasible. Scheme 2 shows the synthetic pathways that were attempted to prepare the trisubstituted product **1**. The palladium catalyzed cross coupling reaction between organoboron derivatives and aryl halides has been extensively used for the synthesis of a wide range of molecules. Both reaction routes 1 and 2 did not proceed with any selectivity and many products were produced. Hunt and coworkers recently reported that the reaction of

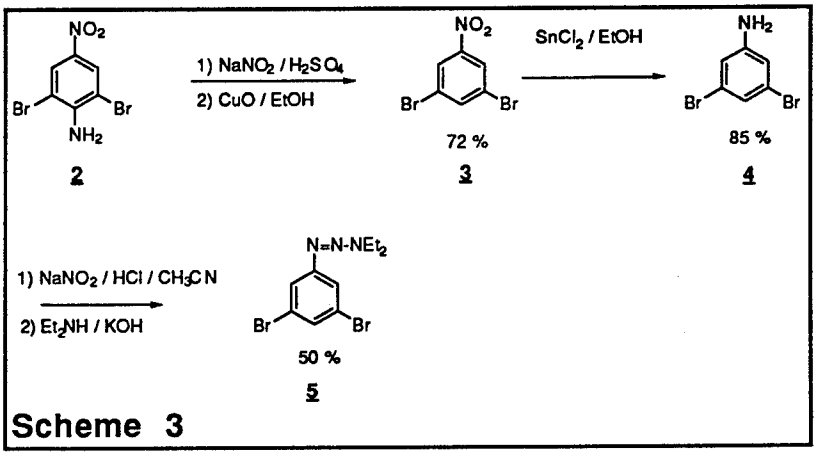
alkenylboronate with aryl halide using palladium catalysts and concluded that these reaction provided a mixture of Heck coupling products and Suzuki coupling products depending on the reaction conditions.[10] Route 3 produced only small quantities of the desired product and its purification was difficult.

Convergent Growth

The large number of functional groups that need to be activated and the difficulties associated with keeping these rigid molecules in solution suggest that growing these molecules via a convergent pathway would increase our probability of success. The synthesis of the stilbene-based dendrimers requires the preparation of an AB_2 monomer for which the B functional groups can first react with the previous generation of dendrons followed by activation of the A moiety to prepare for the next addition of the AB_2 monomer(Scheme 1). After much experimentation and using the lead of both Moore's group[9] as well as the work of Neenan and Miller,[5e] we found that the using a diethyltriazine moiety as the A group produced the highest yields and the most facile way of activating the group for the next round of chemistry. Scheme **3** shows the synthesis of 1-(3,3-diethyltriazine)3,5-dibromobenzene starting from 3,5-dibromo-4-nitroaniline. We also tried using a diazosulfonyl group in place of the diethyltriazine moiety, due to the published facile conversion of this group to an iodo arene bond with KI and 18-crown-6.[11]

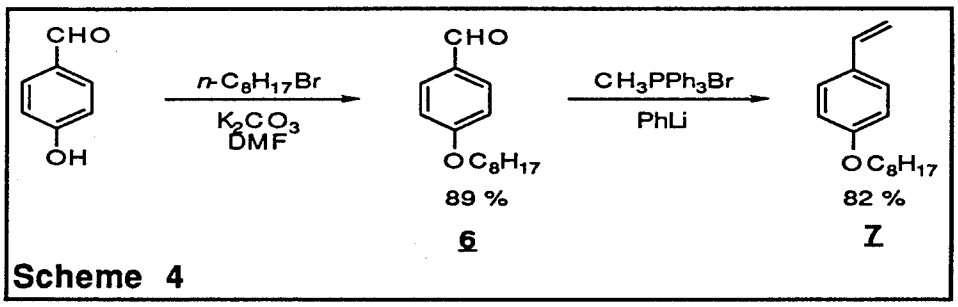
Subsequently, the monomer was found to be unstable to the Heck reaction conditions used during the synthesis of the dendrons.

1-(3,3-diethyltriazine)-3,5-dibromobenzene reacts



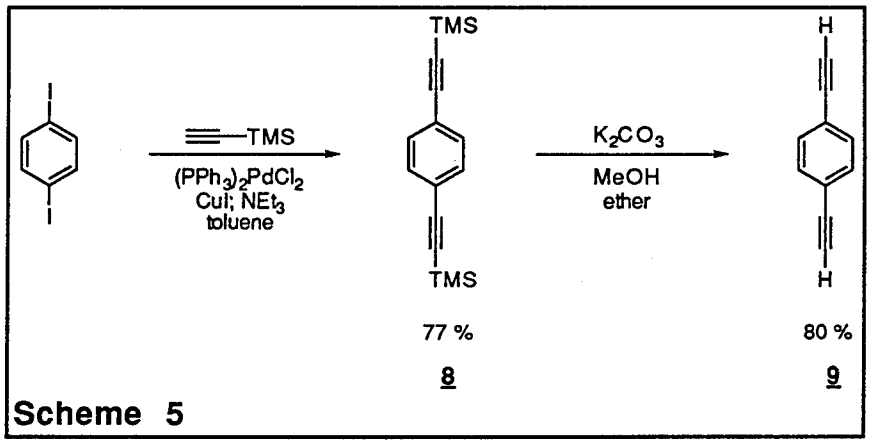
Scheme 3

smoothly with styrene, p-*t*-butylstyrene and p-octyloxystyrene. The synthesis of p-octyloxystyrene is shown in Scheme **4** which starts with the Williamson ether reaction between 4-hydroxybenzaldehyde and 1-bromooctane followed by the conversion of the aldehyde group into a vinyl group via a Wittig reaction.



Scheme 4

The synthesis of our core molecule, 1,4-diethynylbenzene is shown in Scheme **5**. We decided that the synthesis of the diethynyl substituted benzene core would be easier than a divinyl benzene core and it should also have a higher reactivity.



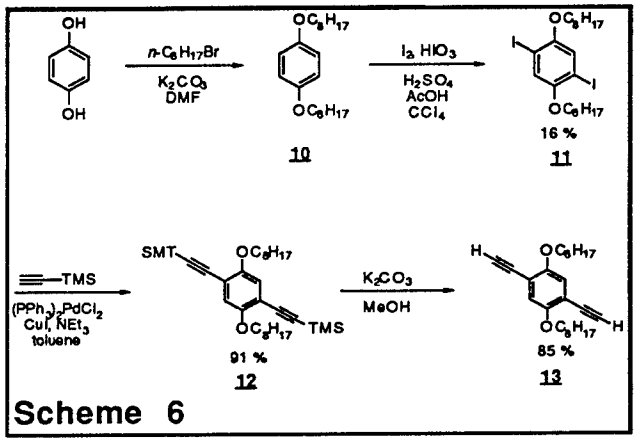
Scheme 5

In this procedure, 1,4-diiodobenzene was first reacted with trimethylsilylacetylene using Pd catalyst, copper iodide and triethylamine and then the TMS groups were removed with K_2CO_3 in methanol to give the desired core molecule.

Styrene was reacted with **5** then reacted further with the core molecule, 1,4-diethynylbenzene but an insoluble product was produced. The product is most likely insoluble due to rigidness of the molecule with the stilbene linkages. A series of modified styrenes were also made (t-Bu and OC_8H_{17} in the para position) and coupled to 1-(3,3-diethyltriazene)-3,5-dibromobenzene in order to try to increase the solubility

of the chain ends. In all cases the result was the same, the coupling product could not be isolated due to its low solubility in the reaction media.

Molecular modeling of the G0 dendrimer helped us to gain a greater understanding for its poor solubility (Figure 2), since even putting solubilizing groups at the chain ends leaves a rigid core that is very difficult to bring into solution. Molecular modeling of an alkyl-substituted core suggested that alkyl groups hanging off the core would act as an internal solvent and thereby increasing the solubility of the whole molecule(Figure **2**). This solution has been effectively used in the preparation of soluble forms of poly(p-phenylene and related polymers.[12] The preparation of the dioctylether substituted core is shown in Scheme **6**.

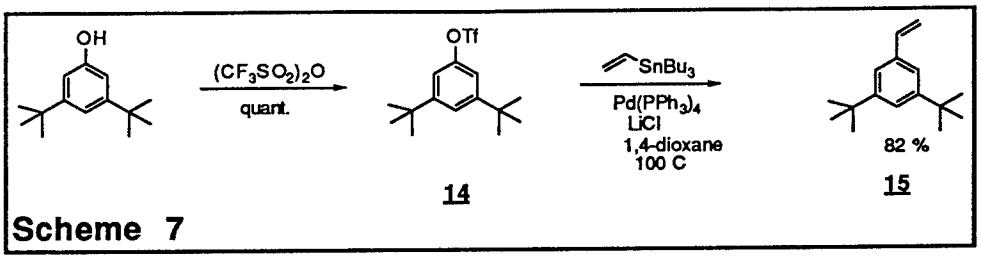


Scheme 6

We also made an attempt to prepare a G1 stilbene dendron, since Moore has reported a great deal of difficulty preparing low generation dendrons due to low solubilities but they found that higher generation dendrons had a greater solubility. The t-butyl substituted G0 dendron was reacted with Bu_3(vinyl)Sn to prepare the vinyl-substitute dendron which was then reacted with 1-(3,3-diethyltriazine)3,5-dibromobenzene. Again this reaction produced an insoluble product.

This result suggested that even greater solubilization of the chain ends was required in order to increase the solubility of the products. Scheme **7** shows the synthesis of 3,5-di-t-butylvinylbenzene which was obtained in high yield starting with 3,5-di-t-butylphenol. The product was then reacted with the 1-(3,3-diethyltriazene)-3,5-dibromobenzene to give the triazine G0 dendron(**19**), which was then activated with

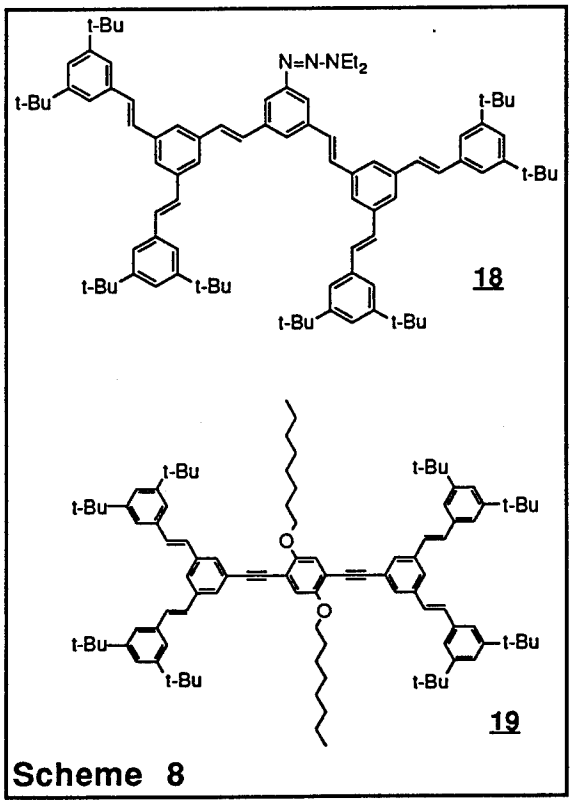
methyiodide. This time the reaction of with the dioctyl-substituted core produced the G0 coupled product.



Scheme 7

A G2 dendron was also produced by first activating the G0-I dendron with tributylvinyltin to produce G0-vinyl. This was then reacted with the 1-(3,3-diethyltriazene)-3,5-dibromobenzene to give G1-triazine(**18**).

Figure 3 shows the UV-vis of G0-I dendron and also the product of the didendron coupled across the diethynyl core. Both the dendron and the coupled product show a peak at 316 nm in the UV but the coupled product also shows a peak at 380 nm which suggests that a conjugation across the core has occurred.



Scheme 8

Experimental Section

General. All palladium catalyzed cross coupling reactions and iodination with iodomethane were performed under an atmosphere of dry nitrigen. All reagents and dry solvents, unless otherwise specified, were obtained from Aldrich Chemical Co. and used without further purification. 4-*tert*-butylstyrene, 1,4-dihydroxybenzene and bis(dibenzylideneacetone)palladium (0) were purchased from Lancaster Synthesis, Inc. Amines and toluene were obtained from Fisher Scientific and purified by distillation over calcium hydride. Dimethylformamide(DMF) was from Fisher Scientific, Inc., dried over molecular sieve 4A and purified by distillation over phosphorus pentoxide in vacuo. Solvents for chromatography were purchased from Fisher Scientific, Inc. and used without further purification. Triethynylbenzene,[12,10] (*E*)-2-phenylethenylboronic acid[13] and (*E*)-ß-styryltributyltin[14] were prepared according to a literature preparation. Melting points were obtained on a Buchi melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker WM-360 spectrometer at 360.13 and 90.56 MHz, respectively or a Varian UNITY300 spectrometer at 299.949 and 75.429 MHz, respectively. Mass spectrometry were recorded on a Finnigan 4500 spectrometer. Analytical TLCs were run on commercial Whatman plates coated with silica gel 60F-254(0.25mm thick). Column and flash chromatography were carried out with Aldrich Silica Gel 60, 70-230 and 200-400 mesh, respectively.

3,5-Dibromonitrobnezene(3). To a mixture of 2,6-dibromo-4-nirtoaniline(40.00 g, 0.135 mol) in glacial acetic acid(140 ml) and concentrated sulfuric acid(40 ml) cooled to 5 °C was slowly added a cold solution of sodium nitrite(10.26 g, 0.145 mol) in concentrated sulfuric acid(60 ml). The temperature was allowed to rise to 18 °C. The mixture was stirred on ice/NaCl bath for 1.5 h and then poured slowly into the cold solution of copper(II) oxide(8.60 g, 0.108 mol) in ethanol(300 ml) while keeping the temperature below 15 °C. The mixture was stirred on ice bath for 1.5 h. A black solid mass was removed by filtration and washed with hot ethanol(200 ml). After removal of the volatiles by evaporation, a tan solid mass was collected by filtration. This solid mass was washed with hot 8N HCl(450 ml, two times) and water until it was no longer acidic. Treatment with activated charcoal in hot ethanol(500 ml) and recrystalization from ethanol provided **3**(27.35 g, 72.0 % yield) as tan needles: mp 100-101.5 °C[lit. 106 °C]; ^{13}C NMR($CDCl_3$) 140.0, 127.9, 125.5, 123.4.

3,5-Dibromoaniline(4). A 500 ml round bottom flask was charged with **3**(23.00 g, 81.88 mmol), tin(II) chloride dihydrate(92.4 g, 0.41 mol) and dry ethanol(140 ml). The mixture was stirred under nitrogen at 75 °C for 40 min, then poured into ice-cold water(200 ml) and adjusted pH to 9 with 10 w/v% sodium hydroxide. Extration with ether(150 ml, six times), drying over magnesium sulfate and concentration provided orange neeldes. Sublimation at 65 °C under 0.13 mmHg provided **4**(17.44 g, 84.9 % yield) as colorless needles: mp 54-55 °C[lit.56.5 °C]; ^{13}C

NMR($CDCl_3$) 148.6, 123.6, 123.3, 116.5.

1-(3',5'-Dibromophenyl)-3,3-diethyltriazene(5). To a mixture of **4**(16.65 g, 66.36 mmol) in 6N HCl(25 ml), acetonitrile(15 ml) and water(10 ml) cooled to -2 °C was added dropwise a solution of sodium nitrite(5.04 g, 73.04 mmol) in water(10 ml) below 0 °C. After stirring at -10 °C for a further 40 min, the mixture was poured into the chilled solution of diethylamine(10.3 ml, 99.56 mmol) in 1M aqueous potassium hydroxide(60 ml) and then stirred at 0 °C for 4 h. Extraction with ether(150 ml, five times) followed by chromatography on SiO_2(247 g) with hexane/ethyl acetate(10/1) provided **5**(11.11 g, 50.0 % yield) as brown oil: ^{1}H NMR ($CDCl_3$)7.50(s, 2H), 7.37(s, 1H), 3.75(br s, 4H), 1.25(br s, 6H); ^{13}C NMR($CDCl_3$) 153.4, 129.7, 122.8, 122.3, 49.2(br), 41.4(br), 14.4(br), 11.1(br).

***p*-Octyloxybenzaldehyde(6).** A 250 ml two necked flask equipped with a dropping funnel and a thermometer was charged with 4-hydroxybenzaldehyde(5.00 g, 40.94 mmol), anhydrous potassium carbonate(8.49 g, 61.43 mmol) and dry DMF(40 ml). The mixture was stirred at 50-60 °C for 20 min and then *n*-bromooctane(7.2 ml, 41.68 mmol) was added dropwise. The mixture was stirred at 70 °C for 16 h. The reaction mixture was poured into water and extracted with ether(150 ml, three times). The organic phase was combined and washed with water(150 ml, three times), dried over magnesium sulfate. Concentration provided **6**(8.58 g, 89.4 % yield) as pale yellow oil: ^{1}H NMR($CDCl_3$) 9.86(s, 1H), 7.82(d, J=8.7 Hz, 2H), 6.98(d, J=8.7 Hz, 2H), 4.03(t, J=6.4 Hz, 2H), 1.89-1.73(m, 2H), 1.54-1.20(m, 10H), 0.89(br t, J=6.3 Hz, 3H); ^{13}C NMR($CDCl_3$) 190.7, 164.2, 131.9, 129.7, 114.7, 68.4, 31.7, 29.2, 29.15, 29.0, 25.9, 22.6, 14.0.

***p*-Octyooxystyrene(7).** A 250 ml four necked flask equipped with a dropping funnel, thermometer, gas inlet and natural rubber septa was charged with methyltriphenylphosphonium bromide(6.71 g, 18.78 mmol) and dry THF(60 ml). The mixture was cooled to -5 °C and then phenyllithium(18 mmol, 10 ml of 1.8M solution in cyclohexane/ether(70/30)) were added dropwise over 15 min below 0 °C. This mixture was stirred at room temperature for 30 min and then cooled to 0 °C. A solution of **6**(4.00 g, 17.07 mmol) in THF(15 ml) was added dropwise over 15 min at 0 °C and the mixture was stirred at room temperature for 2.5 h. After adding a few ml of methanol to hydrolyze the excess reagents, the reaction mixture was poured into water and extracted with ethyl acetate(100 ml, two times). Usual workup and flash chromatography on SiO_2(200 g) with hexane provided **7**(3.25 g, 81.9 % yield) as yellow oil: ^{1}H NMR($CDCl_3$) 7.32(d, J=8.4 Hz, 2H), 6.84(d, J=8.4 Hz, 2H), 6.65(dd, J_{ab}=10.9 Hz, J_{bc}=17.4 Hz, 1H), 5.59(d, J=17.4 Hz, 1H), 5.10(d, J=10.8 Hz, 1H), 3.94(t, J=6.5 Hz, 2H), 1.83-1.70(m 2H), 1.50-1.20(m, 10H), 0.89(br t, J=6.5 Hz, 3H); ^{13}C NMR($CDCl_3$) 159.0, 136.3, 130.2, 127.3, 114.5, 111.3, 68.0, 31.8, 29.3, 29.25, 29.2, 26.0, 22.6, 14.1.

1,4-Bis(trimethylsilylethynyl)benzene(8). A 100 ml Schlenk type reaction flask was charged with 1,4-diiodobenzene(6.60 g, 20.00 mmol), bis(triphenylphosphine)palladium(II) chloride(0.57 g, 0.81 mmol, 4 mol% per 1,4-

diiodobenzene), copper(I) iodide(77 mg, 0.40 mmol, 2 mol%), triethylamine(40 ml) and toluene(20 ml). The mixture was degassed two times and then trimethylsilylacetylene(6.4 ml, 45.29 mmol) was added. The mixture was stirred at room temperature for 3 hr and removal of grey solid mass by filtration, followed by concentration gave brown crude. This crude was taken up into ether(200 ml) and washed with water(50 ml), 10 v/v% HCl(50 ml, two times), 5 w/v% aqueous sodium bicarbonate(50 ml) and water(50 ml). Usual workup of the organic phase, followed by recrystalization from hexane provided **8**(4.17 g, 76.9 % yield) as colorless leaflets: mp 120-121 °C; MS(70 eV) m/z 270(M+), 255(M+-CH_3); ^{1}H NMR($CDCl_3$) 7.39(s, 4H), 0.25(s, 18H); ^{13}C NMR($CDCl_3$) 131.7, 123.2, 104.6, 96.3, -0.4.

1,4-Diethynylbenzene(9). A 250 ml round bottom flask was charged with **8**(4.09 g, 15.12 mmol) and dry methanol(40 ml). The mixture was completely dissolved with dry ether(80 ml) and then anhydrous potassium carbonate(4.18 g, 30.24 mmol) was added. The mixture was stirred at room temperature for 5 h and solid mass was removed by filtration. Concentration and sublimation at 72 °C under 0.34 mmHg provided **9**(1.55 g, 79.7 % yield) as colorless prisms: mp 94-95 °C; ^{1}H NMR($CDCl_3$) 7.43(s, 4H), 3.16(s, 2H); ^{13}C NMR($CDCl_3$) 132.0, 122.6, 83.0, 79.1.

2,5-diiodo-1,4-dioctyloxybenzene (11). A 250 ml two neck flask equiped with a dropping funnel and thermoneter was charged with hydroquoinone (5.00 g, 45.4 mmol), anhydrous K_2CO_3 (15.69 g, 0.114 mmol, 2.5 equiv.) and dry DMF (50 ml). The mixture was stirred at 70 °C for 30 min. and then 1-bromooctane (19.6 ml, 0.113 mmol, 2.5 equiv.) was added. The mixture was stirred at 80 °C for 17 hr. The reaction mixture was poured into water (200 ml) and extracted with ether (100 ml, 6 x). The organic layers were combined and washed with water and dried over $MgSO_4$. Concentration in vacuo gave the mixture of 1,4-dioctyloxybenzene (**10**) and excess 1-bromooctane.

This mixture (9.26 g) was dissolved in CCl_4 (11.0 ml) in a 250 ml round bottom flask equipped with a reflux condensor. To this was added iodine flakes (7.08 g, 27.9 mmol), HIO_3 (3.11 g, 17.7 mmol), 30 v/v % aqueous H_2SO_4 (8.5 ml) and glacial acetic acid (50 ml). The mixture was stirred at 80 °C for 5 hr and cooled with an ice bath. The crystalls were collected by filtration. Washing with a large amount of methanol and drying in vacuo provided **11** (2.71 g, 15.8 % total yield) as pale pink needles: mp 52-53 °C; MS(70 eV) m/z 587(M+); ^{1}H NMR ($CDCl_3$) 7.17 (S, 2H), 3.92 (t, J=6.5 Hz, 4H), 1.88-1.70 (m, 4H), 1.60-1.20 (m, 20H), 0.86 (t, J=6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) 152.9, 122.8, 86.3, 70.4, 31.8, 29.24, 29.21, 26.0, 22.7, 14.1. This compound was used for the next procedure without any additional purification.

2,5-bis(trimethylsilylethynyl)-1,4-dioctyloxybenzene (12). A 100 ml Schlenk flask was charged with **11** (3.24 g, 5.53 mmol), bis (triphenylphosphine) palladium (II) chloride (0.16 g, 0.23 mmol, 4.1 mol % per **11**), CuI (21 mg, 0.11mmol, 2 mol %), triethylamine (20 ml) and dry toluene (10 ml). The mixture was degassed two times and then was stirred at room temperature for 3 hr. Removal of solid mass by filtration and concentration, followed by flash chromatography on SiO_2 with hexane /

ethyl acetate (50/1) provided **12** (2.66 g, 91.3 % yield) as pale yellow needles: mp 65.5 - 66.5 °C; MS (70eV) m/z 527 (M+); ^{1}H NMR ($CDCl_3$) 6.89 (S, 2H), 3.94 (t, J=6.3 Hz, 4H), 1.88-1.70 (m, 4H), 1.60-1.20(m, 20H), 0.86 (t, J=6.6 Hz, 6H), 0.25 (s, 18H); ^{13}C NMR ($CDCl_3$) 154.0, 117.3, 114.0, 101.1, 100.1, 69.5, 31.9, 29.41, 29.38, 29.31, 26.0, 22.7, 14.1, -0.03. This compound was used for the next step without and further purification.

2,5-diethynyl-1,4-dioctyloxybenzene (13). A 100 ml round bottom flask was charged with **12** (2.61 g, 4.96 mmol) and dry methanol (10 ml). This mixure was completely dissolved with dry ether (30 ml) and then anhydrous K_2CO_3 (1.37 g, 9.91 mmol) was added. The mixture was stirred at room temperature overnight. Remmoval of solid mass by filtration followed by recrystallization from CH_2Cl_2-methanol provided **13** (1.61g, 85.1 % yeild) as yellow needles: mp 65-65.5 °C; MS (70 eV) m/z 382 (M+); 1H NMR ($CDCl_3$) ∂ 6.95 (S, 2H), 3.97 (t, J=6.6 Hz, 4H), 3.32 (br, s, 2H), 1.90-1.72 (m, 4H), 1.60-1.20 (m, 20H), 0.89 (t, J=6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$) ∂ 154.1, 117.8, 113.3, 82.4, 79.8, 69.7, 31.8, 29.2, 29.1, 25.9, 22.7, 14.1.

3,5-di-tert-butylphenyl trifluoromethanesulfonate (14). A 250 ml round bottom flask was charged with 3,5-di-tert-butylphenol (6.06 g, 29.4 mmol) and dry pyridine (20 ml). This mixture was cooled with an ice-NaCl bath and trifluormethanesulfonic anhydride (5.5 ml, 33 mmol) was added dropwise. The mixture was stirred on the ice-NaCl bath for an additional 5 min. and then allowed to warm to room temperature and stir for 23.5 hr. The resulting mixture was poured into water and extracted with ether . The combined ether extracts were washed with 10 v/v % HCl, water, and then saturated aqueous NaCl. Drying over $MgSO_4$ and then removing the solvent provided **14** (9.66 g, 97.1 % yield) as pale yellow oil: MS (70eV) m/z 338(M+), 323(M+CH_3); ^{1}H NMR ($CDCl_3$) 7.07 (d, J=1.5 Hz, 2H), 1.33 (s, 18H); ^{13}C NMR ($CDCl_3$) 153.6, 149.8, 122.2, 115.5, 35.2, 31.2. This material was used for the next step without further purification.

3,5-di-tert-butylstyrene (15). A 100 ml Schlenk flask was charged with **14** (9.50g, 28.1 mmol), vinyltributyltin (9.79 g, 30.9 mmol), tetrakis(triphenylphosphine)palladium (0) (0.65 g,).56 mmol, 2 mol % per **14**),LiCl (3.57 g, 84.2 mmol, 3 equiv.) and dry 1,4-dioxane (30 ml). The mixture was degassed two times and stirred at 110 °C for 19 hr. To the reaction mixture was added 1 M aqueous KF (50 ml) and the mixture was stirred at room temperature for 2 hr. The resulting mixture was diluted with ether, filtered and washed with water. Usual workup, followed by careful chromatography on SiO_2 with hexane provided **15** (4.98 g, 82.0 % yield) as a colorless oil: MS(70eV) m/z 216 (M+), 201 (M+CH_3); ^{1}H NMR ($CDCl_3$) 7.35 (br s, 1H), 7.26 (br s, 2H), 6.74 (dd, J_{ab}=10.9 Hz, J_{bc}= 17.5 Hz, 1H), 5.73 (d, J=17.7 Hz, 1H), 5.21 (d, J=10.8 Hz, 1H), 1.33 (s, 18H); ^{13}C NMR ($CDCl_3$) ∂ 150.9, 137.8, 136.8, 122.1, 120.5, 113.0, 34.8, 31.4.

1-{3,5-di-(E)-(3",5"-di tert-butyl)styrlphenyl}-3,3-diethyl triazene (16). A 100 ml Schlenk flask was charged with **5** 3.36 g, 10.0 mmol), **15** (4.74 g, 21.9 mmol, 2.2 equiv.), palladium (II) acetate (45 mg, 0.20 mmol, 2 mol % per **5**, tris-o-

tolylphosphine (0.20 g 0.66 mmol, 6.6 mol %),triethylamine (5.0 ml, 36 mmol), and dry acetonitrile (15 ml). The reaction mixture was degassed two times and then stirred at 105 °C for 45 hr. The reaction mixture was then diluted with ether and filtered. The ether solution was washed with 10 v/v % NH_4CL, water, and saturated aqueous NaCl. Usual workup and flash chromatography on SiO_2 with hexane / ethyl acetate (50/1), followed by recrystallization from hexane provided **16** (2.60 g, 42.8 % yield) as pale orange needles: mp 190.5 - 191.5 °C; MS (70eV) m/z 606 (M+); ^1H NMR ($CDCl_3$) 7.52 (br s, 2H), 7.49 (br s, 1H), 7.40 (br d, J=1.2 Hz, 4H), 7.36 (br s, 2H), 7.25 (d, J=15.9 Hz, 2H), 7.15 (d, J=16.5 Hz, 2H), 3.81 (q, J=7.2 Hz, 4H), 1.37 (s, 36 H), 1.30 (t, J=7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$) 151.8, 151.0, 138.4, 136.7, 129.8, 128.2, 122.0, 121.9, 120.9, 117.6, 43.4 (br), 34.9, 31.5, 10.0 (br).

3,5-di-(E)-(3',5'-di-tert-butyl)styrl-1-iodobenzene (17). A 250 ml Schlenk flask was charged with **16** (2.58 g, 4.26 mmol) and iodomethane (20 ml). The mixture was degassed two times and stirred at 110 °C for 16.5 hr. The reaction mixture was diluted with ether, filtered and concentrated. Flash chromatography on silica with hexane / ethyl acetate (200 /1) provided **17** (2.39 g, 88.6 % yeild) as pale yellow glassy mass: MS (70 eV) m/z 634 (M+); ^1H NMR ($CDCl_3$) ∂ 7.76 (br s, 2H), 7.61 (br s, 1H), 7.38 (s, 6H), 7.19 (d, J=16.2 Hz, 2H), 7.01 (d, J=16.5 Hz, 2H), 1.37 (s, 36 H); ^{13}C NMR ($CDCl_3$) ∂ 151.1, 139.9, 136.0, 133.8, 131.2, 126.2, 124.0, 122.5, 121.0, 95.2, 34.9, 31.5.

Dendrimer G=1; 2,5-bis{3',5'-di-(E)-(3",5"-di-tert-butylstyrl)phenyl}-1,4-dioctyloxybenzene (18). A 100 ml Schlenk flask was charged with **13** (0.20 g, 0.52 mmol), **17** (1.01 g, 1.60 mmol), bis(triphenylphosphine)palladium(ii) chloride (22 mg, 0.031 mmol, 6 mol % per **13**), di-i-propylamine (2.0 ml, 14 mmol) and dry THF (15 ml). The mixture was degassed two times and then CuI (6 mg, 0.031 mmol) was added. This mixture was stirred at room temperature for 9 hr. The reaction was poured into water and extracted with ether. The ether solution was washed with saturated aqueous NH_4Cl, dried over $MgSO_4$ and concentrated. Flash chromatography on silica with hexane / CH_2Cl_2 (4 /1) provided **18** (513 mg, 70.2 % yield) as greenish powder: ^1H NMR ($CDCl_3$) 7.67-7.60 (m, 6H), 7.43-7.36 (m, 12H), 7.25 (d, J=16.2 Hz, 2H), 7.11 (d, J=16.8 Hz, 2H), 7.08 (s, 2H), 4.09 (t, J=6.6 Hz, 4H), 1.98-1.84 (m, 4H), 1.68 - 115 (m, 96H), 0.79 (t, J=6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$) 153.8, 151.1, 138.2, 136.3, 130.8, 128.3, 127.1, 124.7, 124.1, 122.4, 121.0, 117.2, 114.1, 94.8, 86.0, 69.8, 34.9, 31.8, 31.5, 29.4, 29.3, 26.1, 22.6, 14.0.

Triazene dendrin G=2; 1-[3',5'-di-(E)-{3',5'-di-(E)-3''',5'''-di-tert-butylstryl}phenyl}-3,3-diethyltriazene (19). A 250 ml Schlenk flask was charged with **5** (0.54 g, 1.61 mmol), **17** (1.99 g, 3.73 mmol), pallidium (II) acetate (15 mg, 0.067 mmol, 4.2 mol %), tris-o-tolylphosphine (98 mg, 0.32 mmol, 20 mol %), triethylamine (1.0 ml, 7.2 mmol), and dry acetonitrile. The mixture was degassed two times and stirred at 110 °C for 42 hr. The reaction mixture was diluted with ehter and filtered. The ether solution was sashed with 10 v/v % HCl, water, and saturated aqueous NaCl. Flash chromatography of the product on silica with hexane / CH_2Cl_2

(40 / 1) provided **19** (1.25 g, 62.7 % yield) as a yellow glassy mass: ^{1}H NMR ($CDCl_3$) 7.63 (br s, 4H), 7.58 (br s, 2H), 7.55 (br s, 1H0, 7.43 (d, J=1.2 Hz, 8H), 7.40 (d, J=1.5 Hz, 4H), 7.29 (br s, 2H), 7.291 (d, J=16.5 Hz, 6H0, 7.17 (d, J=16.2 Hz, 6H), 3.67 (q, J=6.9 Hz, 4H), 1.50-1.20 (m, 78 H); ^{13}C NMR ($CDCl_3$) 152.0, 151.1, 151.0, 138.3, 138.2, 138.1, 136.5, 130.2, 129.3, 128.7, 127.8, 123.9, 123.7, 122.2, 121.0, 118.1, 34.9, 31.5.

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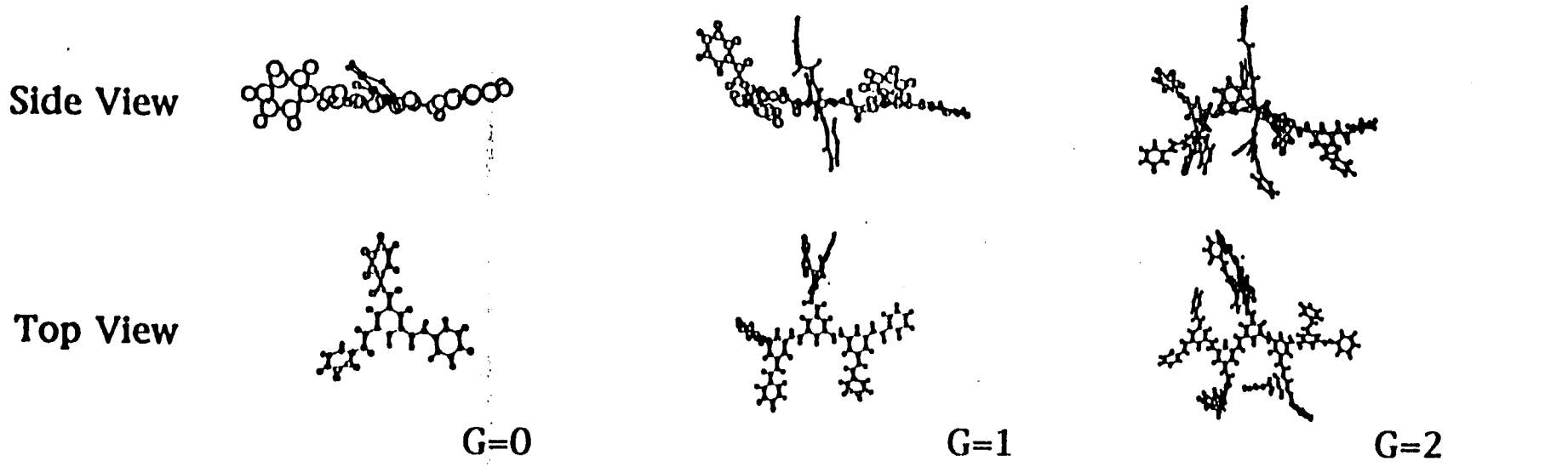
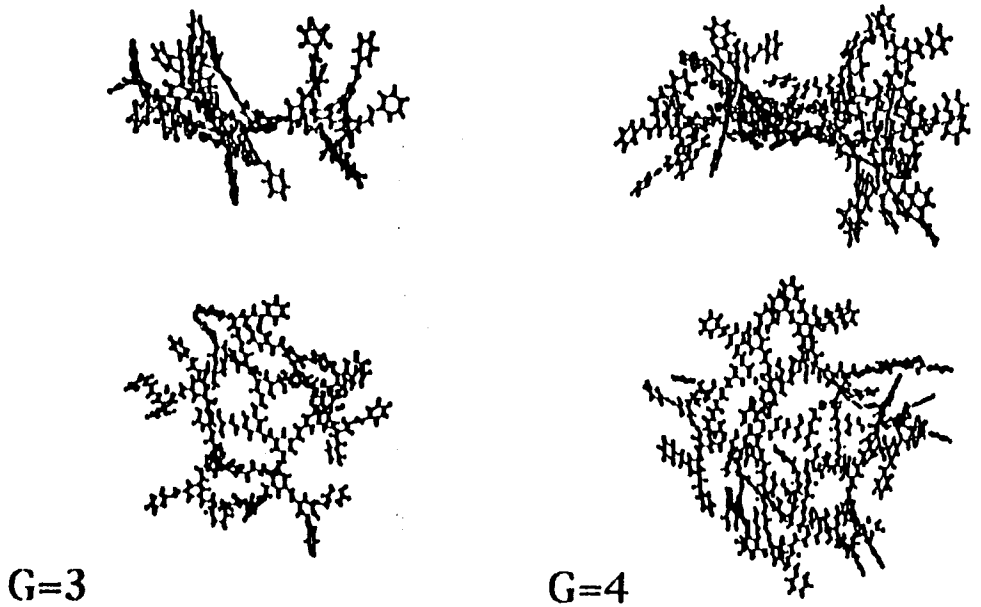
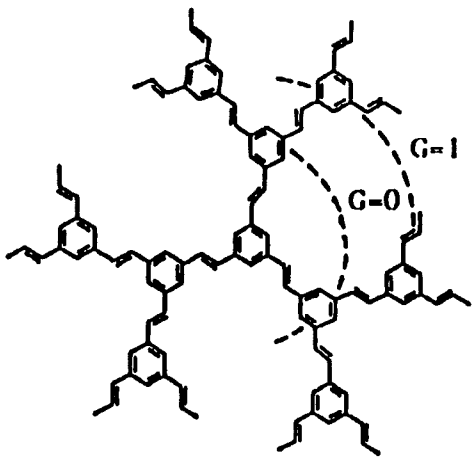


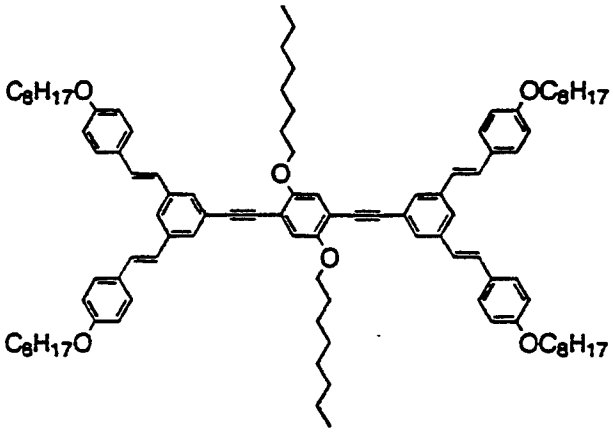




Stilbenoid Dendritic Molecule 1

Figure 1.

Figure 2.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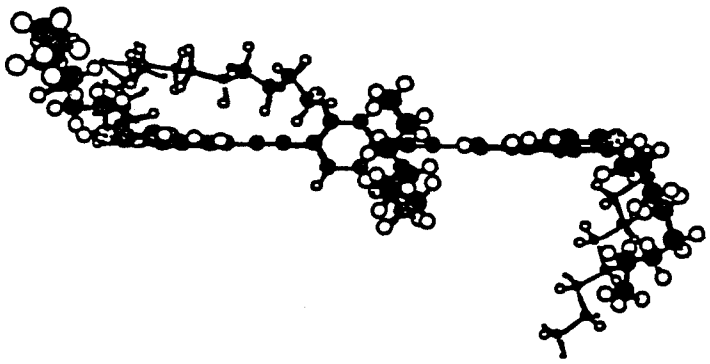

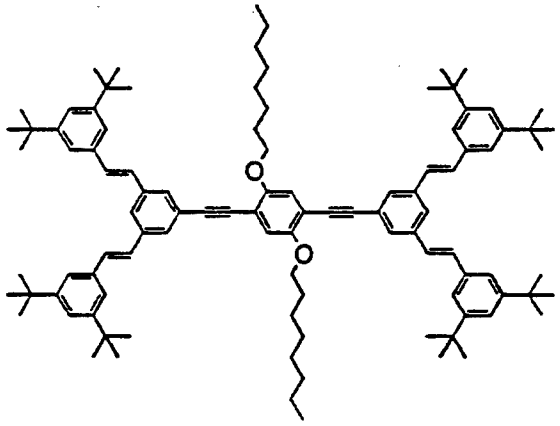
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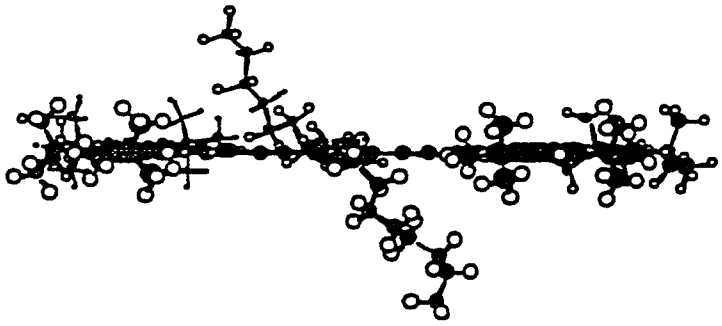

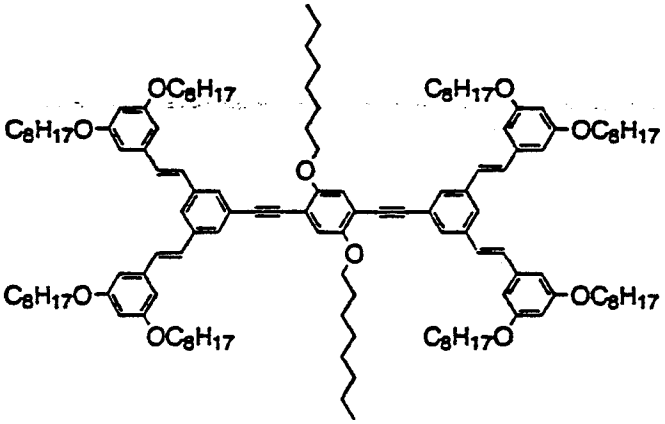
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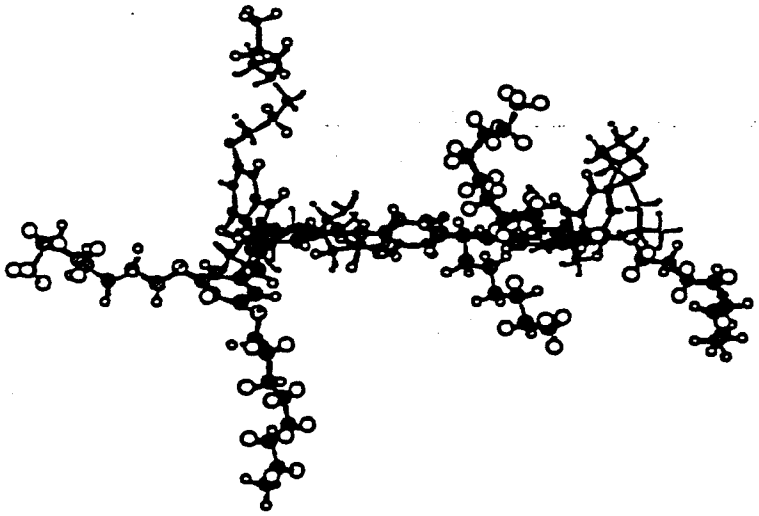
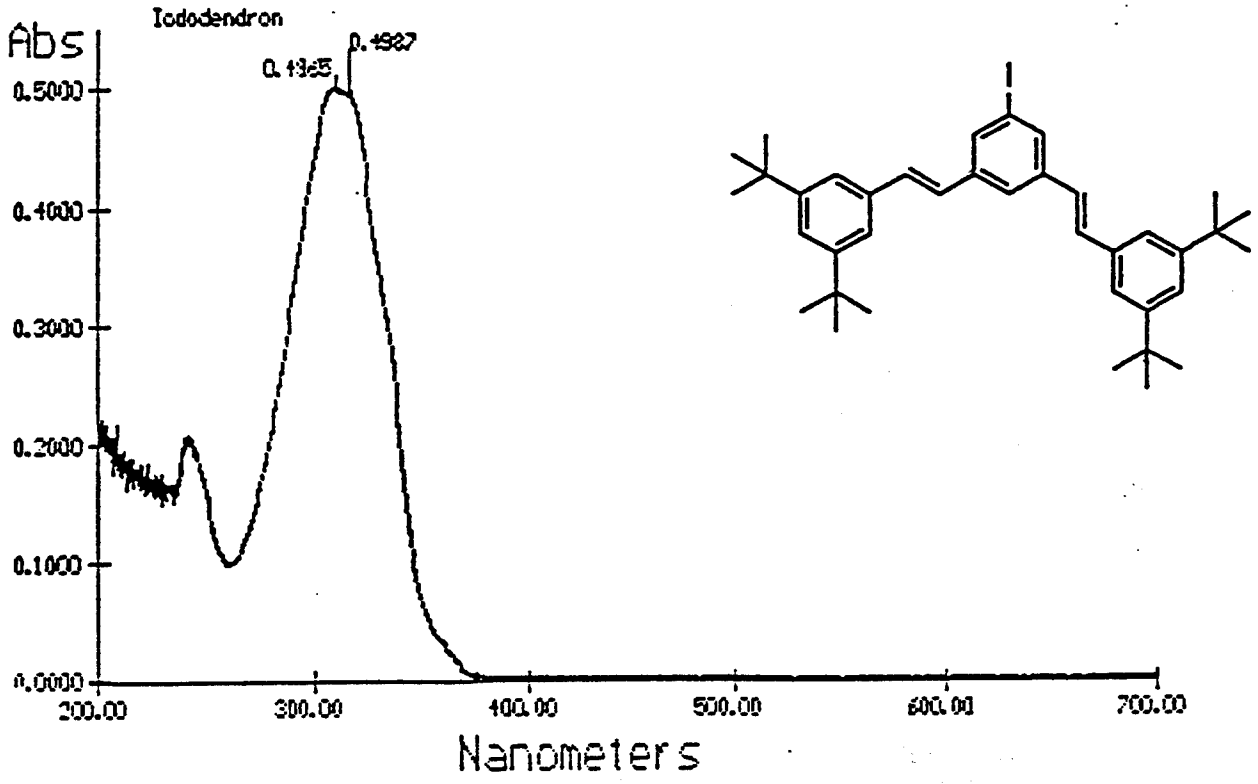


Figure 3.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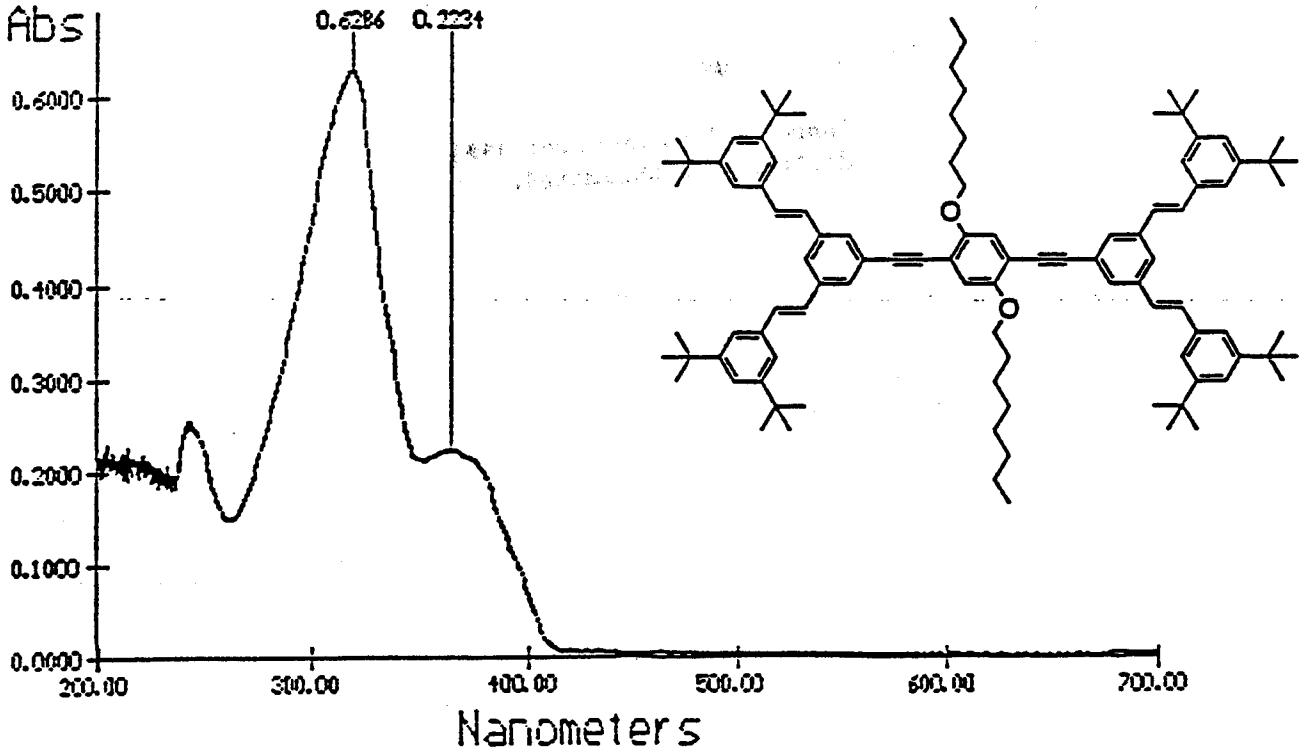
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