

Effect of generation on the electronic properties of light-emitting dendrimers

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ABSTRACT

We have compared the optical and electronic properties of a series of porphyrin centred dendrimers containing stilbene dendrons. The first and second generation dendrimers could be spin-coated from solution to form good quality thin films. Incorporation into single layer light-emitting diodes gave red-light emission with maximum external quantum efficiencies of 0.02% and 0.04% for the first and second generation dendrimers respectively. We have determined by photoluminescence studies that energy can be transferred efficiently from the stilbene dendrons to the porphyrin core and that PL emission is from the core. Cyclic voltammetry studies on the dendrimers show that the reductions are porphyrin centred with the dendrons only affecting the rate of heterogeneous electron transfer between the electrode and the dendrimers. This suggests that charge mobility within a dendrimer film in an LED will be affected by the porphyrin edge to porphyrin edge distance. We have studied the hydrodynamic radii of the dendrimers by gel permeation chromatography and found as expected that the average porphyrin edge to dendron edge distance increases with generation. This is consistent with the slowing of heterogeneous electron transfer observed in the cyclic voltammetry on increasing the generation number and suggests that the dendrons are interleaved in the solid state to facilitate charge transport.

Keywords: Dendrimer, light-emitting diode, cyclic voltammetry, hydrodynamic radii

1. INTRODUCTION

Organic light-emitting materials for use in light-emitting diodes (LEDs) have generally fallen into two classes; molecular^{1,2} or polymeric^{3,4}. More recently there have been a few reports of light-emitting dendrimers which have been successfully used in LEDs.^{5,6} Dendrimers consist of three main components, the core, the dendrons, and the surface groups. In higher generation dendrimers it is only the surface groups which come in contact with the environment as steric interactions within the dendrons cause the dendrimer to become "spherical". The fact that only the surface groups may be in contact with the environment gives rise to one of the potential advantages of dendrimers over polymers and molecular materials. With polymers and molecular materials a change in functionality to change the electronic properties of the material can often lead to a change in the physical and processing properties of the material relative to the parent compound. With dendrimers, if only the surface groups are in contact with the solvent then the electronic properties on the inside of the dendrimer should be alterable without changing the processing properties, that is, their electronic properties and processing requirements can be disengaged. Most of the studies of dendrimers containing electroactive moieties have them connected by saturated units.^{7,8} A potential disadvantage of using dendrimers with a large proportion of saturated units in LEDs is that the saturated components are insulators and could inhibit charge mobility in a film. This could be overcome by having the dendrons and core containing all unsaturated units. There have been two types of "conjugated" dendrimers described which contain phenylacetylene⁶ or stilbene dendrons.^{5,9-11} One of the aspects of design in unsaturated dendrimers is to have the HOMO-LUMO energy gap of the dendrons larger than that of the core. This should have the effect of funnelling energy which has been injected into the dendron to the core. In the case of a radical anion or cation this would trap the charge at the core of the dendron in a manner akin to a two layer LED which contains both a hole transporting emitting layer and an electron transport layer. To this end we have developed a series of dendrimers which consist of lipophilic surface groups (3,5-*t*-butylphenyl), conjugated dendrons (stilbenes) and luminescent cores [*e.g.*, distyrylbenzene (figure 1)].^{5,9} Whilst at first sight these dendrimers appear fully conjugated, the fact that the stilbene linkages are in a *meta* arrangement around the benzene rings means that to a first approximation the individual chromophores can be considered electronically independent. For example, the distyrylbenzene dendrimer in Figure 1 shows photoluminescence spectra corresponding essentially to the distyrylbenzene core and not the whole of the dendrimer.⁵

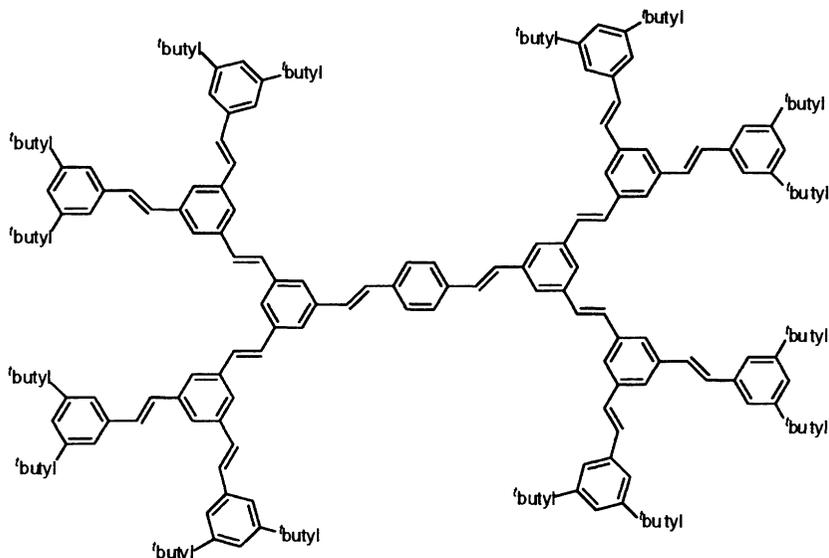


Figure 1 Second generation distyrylbenzene dendrimer.

In the case of the distyrylbenzene cored dendrimers we produced three generations of dendrimers and found that whilst all three generations could be processed from solution to give good quality thin films their properties when incorporated into light-emitting diodes were remarkably different. Most striking was the fact that the efficiency of a single layer LED (ITO/dendrimer/Ca) could vary up to nine-fold depending on the dendrimer generation.⁵ In addition, the emission spectrum was observed to differ depending on the generation. In this paper we describe the properties of a second family of dendrimers which have the same surface groups and dendrons but contain porphyrin cores. These porphyrin centred dendrimers are of particular interest as red-light emitting materials.

2. RESULTS AND DISCUSSION

The synthesis of the porphyrin dendrimers, illustrated in Figure 2, is reported in detail elsewhere.⁹

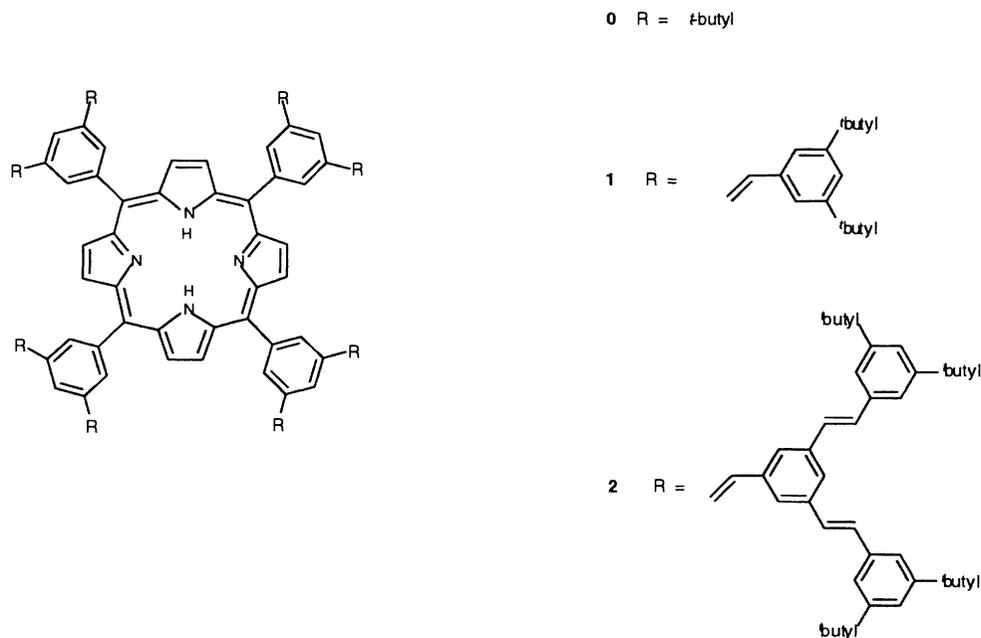


Figure 2 The “zeroeth” (0), first (1), and second (2) generation dendrimers.

The porphyrin dendrimers are not planar as illustrated in Figure 2. The dendrons are held orthogonally to the core because of steric interactions between the phenyl rings and the β -pyrrolic protons. Both the first, 1, and second generation, 2, dendrimers could be spin-coated from solution to give good thin films. Single layer LEDs were prepared by spin-coating the dendrimers from solution onto ITO on glass substrates. The devices were then completed by evaporating either calcium or aluminium cathodes. The electroluminescence emission spectrum of 1 is shown in Figure 3 with emission from the second generation dendrimer 2 being essentially the same. The emission spectrum has peaks at 677 nm and 729 nm which correspond to two singlet emission peaks. These are slightly red shifted when compared to the solution photoluminescence spectra of 1 and correspond to the Q(0,0) and Q(0,1) transitions. From the emission spectrum the Commission Internationale d'Éclairage 1931 (C.I.E.) co-ordinates for 1 were determined to be (0.69, 0.30). This corresponds to a good red emission, in fact more red than is required for a full colour display. These results clearly illustrate two points with regard to the use of dendrimers. First, the porphyrins processing properties have been enhanced by being incorporated into the dendritic structure and second, the π - π stacking of the porphyrins, which normally quenches luminescence in the solid state, has been avoided.

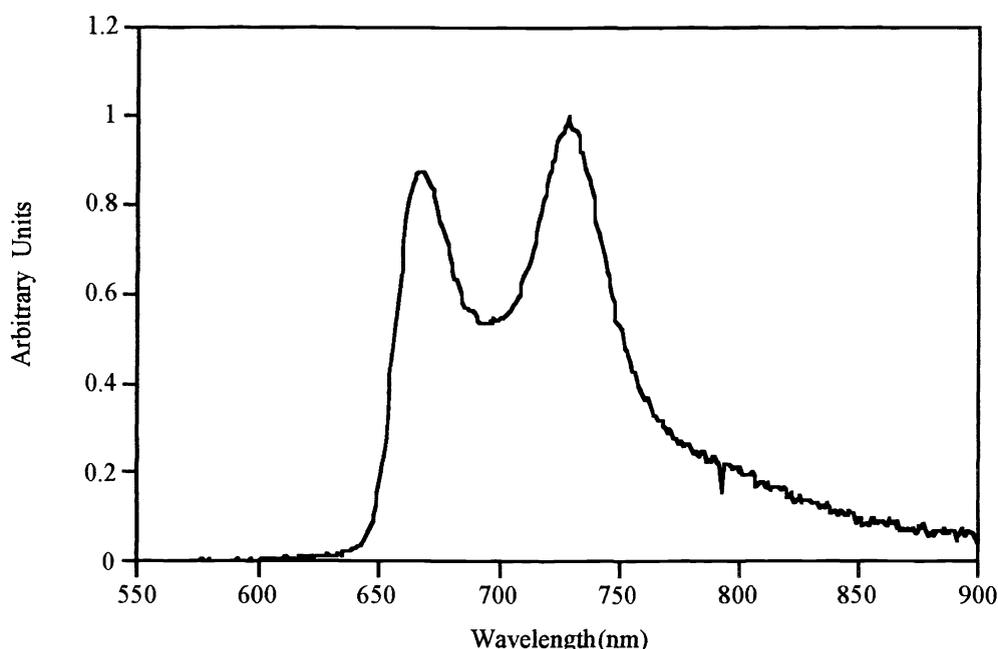


Figure 3 Electroluminescence spectra for an LED consisting of ITO/1/Ca

We found that with calcium electrodes the first generation dendrimer had an external quantum efficiency of 0.02% whilst for the second generation the efficiency was 0.04%. In addition, changing the cathode to aluminium effected little change in the external quantum efficiencies of the two dendrimers suggesting that electron injection may not be the limiting factor. The fact that only a two fold increase was observed for the LED efficiency in going from the first to second generation dendrimer prompted the question as to how charge is injected and how energy may be transferred through these materials.

The first question that we wished to answer was whether energy could be transferred from the dendrons to the core given that they were being held orthogonally to the core. We excited the dendrimers in solution at 300 nm (corresponding to the dendron absorption) and 420 nm (the porphyrin Soret absorption) and in both cases only observed emission from the core.⁹ This clearly shows that energy is transferred from the dendrons to the core. To get a feel for the efficiency of transfer of the excited state from the dendron to the core we carried out a photoluminescence excitation experiment and found that the energy transfer occurred with almost 100% efficiency.

However, in an LED we are not introducing singlet excited states but rather the material near the anode is being oxidised (hole injection) to form radical cations and dication or reduced (electron injection) near the cathode to form radical anions or

dianions. The question that therefore arises is whether the holes or electrons are injected into the dendrons with those charges then being funnelled to the porphyrin core before meeting the opposite charge, forming a singlet exciton, and subsequently emitting light, or whether the charges are injected directly to the core. One way of determining this is by using cyclic voltammetry. One of the important issues in cyclic voltammetry is the heterogeneous electron transfer between the electrode and the substrate. In other porphyrin dendrimer systems it has been observed that if the distance from the electrode to the electroactive species is greater than 10 \AA then the redox process can be significantly slowed,¹² with broadening and reduction in size of the anodic and cathodic peaks¹³. With the relative rigid structures of **1** and **2** the porphyrin core will be held a defined distance away from the electrode by the dendrons. If the distance from the porphyrin core to dendron edge is greater than that allowed for electron transfer from the electrode to the core then we would expect to see either oxidation or reduction of the dendrons on an anodic or cathodic sweep respectively with rapid transfer of the charge to the porphyrin core. The potential at which the dendrons will be oxidised or reduced should be independent of dendron size due to the *meta* arrangement of the stilbene units and we would therefore expect to see similar redox processes for each generation. The alternative case that needs to be considered is when the core is close enough to the surface of the dendrimer for direct electron transfer from the electrode to the core. In this case the redox properties of the porphyrin core would be observed and we would expect to see a difference in the redox potentials with a change in generation.^{12,13} With dendrimers **0**, **1** and **2** the difference should be easily observed as the stilbene dendrons should be more difficult to reduce or oxidise than the porphyrin core. The redox properties of simple porphyrins are well understood. Porphyrins undergo two one electron oxidations to form a radical cation and dication respectively. They are also capable of being reduced twice with two one electron reductions to form a radical anion and subsequent dianion.¹⁴ We carried out cyclic voltammetry studies on the “zeroth,” first, and second generation porphyrin dendrimers and the results of the reduction cyclic voltammograms are shown in Figures 4, 5, and 6.

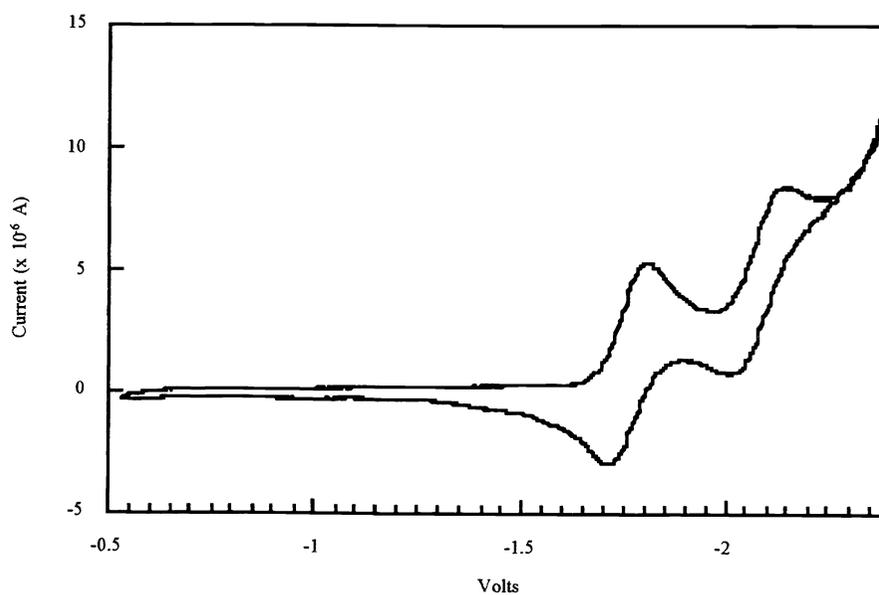


Figure 4 Reduction cyclic voltammogram of **0** (Scan rate = 35 mVs^{-1})

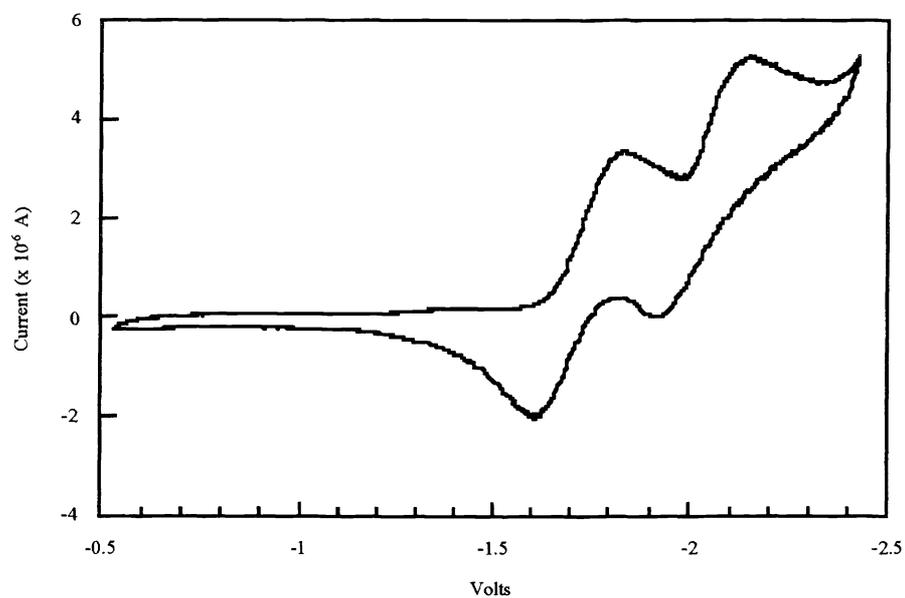


Figure 5 Reduction cyclic voltammogram of **1** (Scan rate = 35 mVs⁻¹)

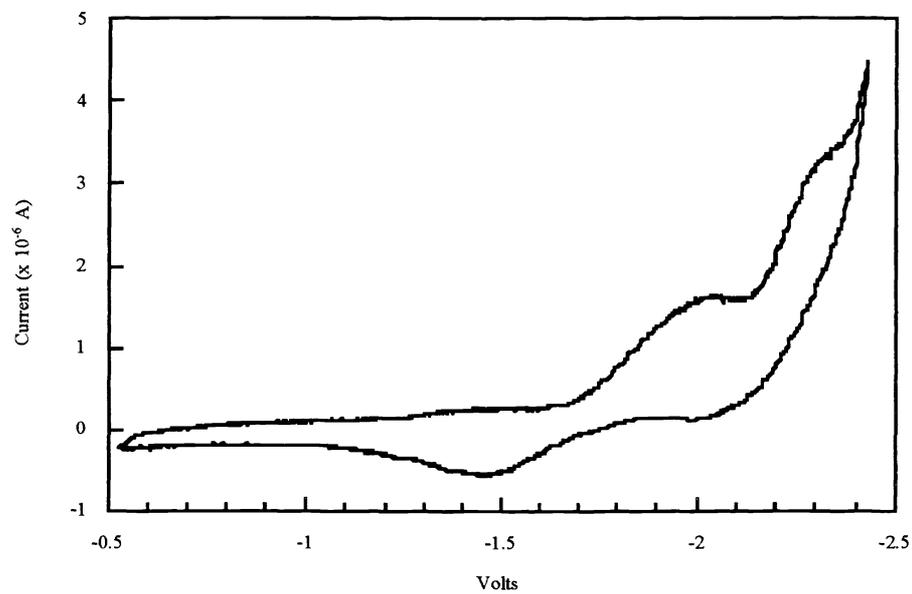


Figure 6 Reduction cyclic voltammogram of **2** (Scan rate = 35 mVs⁻¹)

For the “zeroeth” generation porphyrin **0** two chemically reversible one electron porphyrin centred reductions are clearly observed (Figure 4). These reductions are quasi-reversible as the difference between the cathodic and anodic peaks is greater than 57 mV.¹⁵ Similarly both the first and second generation dendrimers, **1** and **2**, have two chemically reversible one electron porphyrin centred reductions. Again the reductions are only quasi-reversible (the reduction data is summarised in table 1). There are a number of important features in the cyclic voltammograms. First, the only reduction processes that we observed are porphyrin centred indicating that heterogeneous electron transfer is occurring directly between the electrode and porphyrin core and not via the dendrons. The second point to note is that the $E_{1/2}$ s of the first and second reductions of all three dendrimers are essentially at the same voltage with respect to the ferrocenium/ferrocene couple. This indicates that the dendrons are not having an influence on the electronic environment of the porphyrin core. This can be compared to porphyrin centred dendrimers with polyether-amide dendrons attached to the 2,6-positions of phenyl groups connected to the *meso*-positions of the porphyrin. With these latter porphyrin dendrimers the oxidation of the porphyrin ring occurred at less positive potentials whilst the reductions occurred at more negative potentials as the generation number increased. This was being explained as being a result of the increasingly electron rich microenvironment near the porphyrin provided by the dendrons.¹²

Table 1 Reduction potentials for the three dendrimers

Dendrimer	$E_{pc}(r1)/V$	$E_{pa}(r1)/V$	$E_{1/2}(r1)/V$	$E_{pc}(r2)/V$	$E_{pa}(r2)/V$	$E_{1/2}(r2)/V$
0	-1.80	-1.71	-1.76	-2.14	-2.01	-2.08
1	-1.84	-1.60	-1.72	-2.15	-1.92	-2.04
2	-2.04	-1.46	-1.75	-2.34	-1.99	-2.17

The final point to note is that the anodic and cathodic peaks become more separated for both reductions in going from “zeroeth” to the second generation dendrimer. This is indicative of slow heterogeneous electron transfer between the electrode and the dendrimers and is similar to that observed in other higher generation porphyrin centred dendrimers. The conclusion that can be drawn from the electrochemistry is that in solution the dendrons do not play a role in the transport of charge to the porphyrin core. This is an important observation as it suggests that charge transport through a dendrimer film occurs by hopping of the charge from one porphyrin core to the next. Given that the dendrons could act as a barrier to that approach it is therefore important to determine the size of the dendrimers and how close the porphyrin cores can approach one another.

To get a feel for the size of the dendrimers we determined the hydrodynamic radii of the porphyrin dendrimers using gel permeation chromatography (gpc) against polystyrene standards. The separation of molecules in a gpc column is due to differences in the hydrodynamic volume of the molecules. We have assumed that the hydrodynamic volume of a dendrimer is the same as the hydrodynamic volume of a polystyrene standard with the same elution time. To calculate the hydrodynamic radii of the porphyrin dendrimers we have utilised the Hester-Mitchell equation¹⁶ (equation 1) which gives the diameter in terms of gpc viscosity molecular weight and intrinsic viscosity,

$$D_h = (240/\pi N_A)^{1/3} (\bar{M}_v [\eta])^{1/3} \quad (1)$$

where D_h = Hydrodynamic diameter (in cm), \bar{M}_v = Viscosity molecular weight, $[\eta]$ = Intrinsic viscosity (in dLg^{-1}), and N_A = Avogadro's number. To determine the intrinsic viscosity measurements from the gpc we used the Mark-Houwink relationship, $[\eta] = K \bar{M}_v^\alpha$ as the constants K and α are known to be $14 \times 10^{-5} \text{dLg}^{-1}$ and 0.7 respectively for polystyrene in tetrahydrofuran at 25 °C.¹⁷

The gpc analysis of the three compounds was carried out in tetrahydrofuran at 25 °C and the \bar{M}_v s were determined to be 1131 for **0**, 2742 for **1**, and 4856 for **2**. Using the two equations these \bar{M}_v s correspond to an average hydrodynamic radius increasing from 7 Å for **0** to 12 Å and 16 Å for **1** and **2** respectively. The question that then arises is how the radii relate to the structure of the dendrimers. To do this we have used Chem 3D to roughly calculate the interatomic distances for the first and second generation dendrimers (the measurements are illustrated for **2** on Figure 7). To do this we have assumed that the dendrons are orthogonal to the core and the measurements we have taken are from carbon nucleus to carbon nucleus which does not take into account Van der Waals radii and the protons at the surface. From this structure it can be seen that some of the surface groups of the dendrons of **2** are directed back over the porphyrin ring and this has been confirmed by ¹H n.m.r. studies.⁹

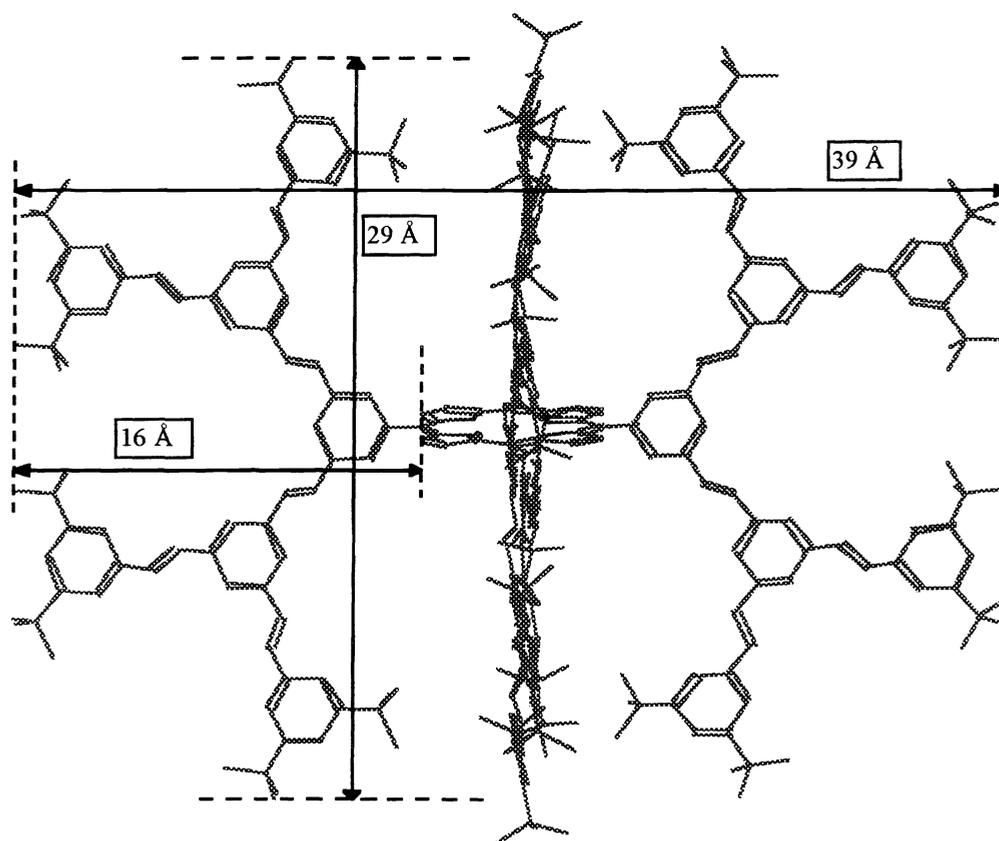


Figure 7 Structural measurement taken for 2.

From the measurements in Figure 7 the geometric mean distance from the centre of the porphyrin core of 2 to the surface-*t*-butyls was determined to be ≈ 18 Å which was close to that observed by gpc. Given that the radius of the porphyrin (from the centre to the *meso* position) was ≈ 3.5 Å this means that if dendrimer 2 acted as touching spheres the porphyrin to porphyrin distance would be between ≈ 30 - 32 Å. Hence it would be unlikely that electron transfer could occur from porphyrin to porphyrin in a film as the electrochemistry shows that heterogeneous electron transfer was already impeded from an electrode when the dendrimer surface to porphyrin edge is ≈ 16 Å. This therefore suggests that the dendrons of the dendrimer are interleaved thus bringing the porphyrin cores closer together. Space filling models can give an illustration of the three dimensional shape of molecules and two different views of the second generation dendrimer are shown in Figure 8.

As can be seen in Figure 8, the dendrons of 2 prevent close face to face packing of the porphyrin cores due to the dendrons overlapping the top of the porphyrin rings. Therefore, the only way that porphyrin cores could easily be close enough for direct transfer of charge from one porphyrin ring to another was for the dendrons to interleave with the porphyrins arranged edge to edge. The limit in the approach of two porphyrins in two different dendrimers was governed by the radius of the dendrons. As the dendrons are interleaved it might be expected that π - π stacking of the dendrons could occur which could change their electronic properties relative to that measured in solution. However, we observed no change in the U.V.-visible absorption spectra of the dendron component in going from solution to the solid state. This was consistent with little or no π - π stacking of the dendrons. For the first generation dendrimer 1 a similar argument can be followed. The radius of the dendrons from porphyrin centre to dendron surface in the plane of the porphyrin was determined to be ≈ 14 Å and perpendicular to the plane of the porphyrin ≈ 9 Å. This gave an average radius of ≈ 12 Å which was similar to the hydrodynamic radius measured by gpc. This again means that for electron transfer to occur directly from porphyrin core to porphyrin core the dendrons must be interleaved. This suggests that one of the reasons for the poor external quantum efficiencies of LEDs based on these porphyrin dendrimers may be due to poor charge mobility in the films with the limiting factor direct charge transfer from porphyrin ring to porphyrin ring. The above arguments are based mainly on data from the structures in solution rather than the solid state. However, we do not believe that there will be a significant structural change

in the dendrimers in going from solution to the solid state for two reasons. First, the dendrons are orthogonal to the core due to the steric interactions of the β -pyrrolic protons with the *meso*-phenyl attached directly to the porphyrin ring and this will be similar both in solution and the solid state, and second, as described above there is no change in the absorption spectra of the dendrons in going from the solution to the solid state indicating that they are still in plane with the *meso*-phenyl substituent.

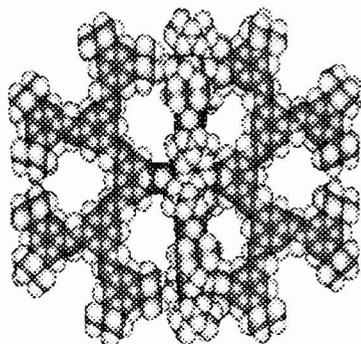
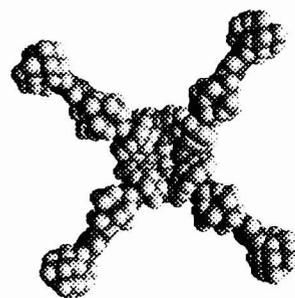


Figure 8a Space filling model of 2 viewed from the porphyrin edge



8b Space filling model of 2 viewed orthogonally to the porphyrin plane

3. CONCLUSION

We have studied a new family of electroluminescent dendrimers which contain *t*-butyl surface groups, stilbene dendrons, and porphyrin cores. We have found that LEDs could be prepared and that the electroluminescence is red. Cyclic voltammetry indicated that electrons were injected directly into the porphyrin core and not via the dendrons. Comparing the electrochemical results with the hydrodynamic radii of the dendrimers suggests that in the solid state the dendrons of the dendrimers are interleaved but there was still a significant distance between the porphyrin rings in adjacent dendrimers. This may give rise to poor electron transfer and limit the charge transport in this family of materials. These effects are currently under further investigation.

4. EXPERIMENTAL

The electrochemistry was performed using an EG&G Princeton Applied Research potentiostat/galvanostat model 236A. All measurements were done at room temperature, in freshly distilled dichloromethane with 0.1 M tetra-*n*-butylammonium tetrafluoroborate as the supporting electrolyte. A glassy carbon working electrode, platinum wire counter electrode, and a Ag/AgCl/NaCl (saturated) reference electrode were used. The solutions were deoxygenated by saturation with argon. The standard used was the ferrocenium/ferrocene couple.¹⁸ The tetra-*n*-butylammonium tetrafluoroborate was purified by recrystallisation from an ethylacetate/diethylether mixture and dried under vacuum. The dichloromethane was purified by a literature procedure and freshly distilled from calcium hydride.¹⁹ Gel permeation chromatography was carried out using PLgel 3 μ m Mixed-E columns (300 mm, 7.5 mm diameter) from Polymer Laboratories calibrated with polystyrene narrow standards ($\overline{M}_p = 580-20.6 \times 10^3$) in tetrahydrofuran with toluene as flow marker. The tetrahydrofuran was degassed with helium and pumped at a rate of 1 mL/min at 25°C.

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