The effect of intermolecular interactions on the electro-optical properties of porphyrin dendrimers with conjugated dendrons

Michael J. Frampton, Steven W. Magennis, Jonathan N. G. Pillow, Paul L. Burn and Ifor D. W. Samuel

aThe Dyson Perrins Laboratory, Oxford University, South Parks Road, Oxford, UK OX1 3QY
bOrganic Semiconductor Centre, School of Physics and Astronomy, University of St Andrews, North Haugh, St Andrews, Fife, UK KY16 9SS

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We have synthesised a new family of dendrimers with stilbene dendrons attached to a porphyrin core via a stilbene unit and compared their properties with a family of dendrimers with the same core and dendrons but with the dendrons attached via a phenyl unit. The oxidation and reduction half potentials of the two dendrimer families were found to be the same and independent of generation indicating that the dendrons were not creating a micro-environment for the core. However, the rate of heterogeneous electron transfer was found to be strongly dependent on link type and generation. The photoluminescence quantum yield (PLQY) of the dendrimers was also found to be strongly dependent on the method of attachment of the core. In solution the dendrimers with the stilbene link between core and dendrons had PLQYs 1.5 times higher than their phenyl counterparts but in the solid state the trend was reversed with the phenyl linked dendrimers generally having a higher PLQY. The difference in properties has been assigned to the comparative openness of the dendrimer architectures and the effect of the dendrons on the shape of the porphyrin core.

Introduction

Functional dendrimers that contain the active component at the core of the dendrimer are becoming increasingly studied. The dendritic architecture provides an elegant method of controlling the intermolecular interactions of the active core. The control is achieved at three levels; first, the nature of the dendron attached to the core, second the number of dendrons attached to the core, and finally the generation of the dendron. Dendrons can be divided into two main types, those that contain conjugated links between the branching points and those that have saturated links. It is not surprising that dendrimers with the same core but different dendron types, saturated or unsaturated, would give rise to dendrimers with different properties.1 One of the more widely studied families of dendrimers are those in which the core is comprised of a porphyrin. Most of these studies have utilised flexible dendrons with saturated links between the branching points.2–5 In such dendrimers the nature of the dendron and generation have had a strong influence on the photophysical and redox properties of the porphyrin core. However, these studies have tended to be carried out in solution and little is known about the effect of the dendrimer structure on the porphyrin cores in the solid state. In contrast to the studies on porphyrin cored dendrimers with saturated links there have been fewer publications of porphyrin cored dendrimers with conjugated dendrons, with stilbene6 and phenylene7,8 based dendrons having been reported. Our interest in porphyrin cored dendrimers has arisen from the reports that porphyrins can be used as red light-emitters in organic light-emitting diodes (OLEDs).9–11 Porphyrins have a propensity to \( \pi \)-stack and be non-luminescent in the solid state. In OLED devices this problem is generally overcome by incorporating the porphyrins as a guest in a blend at low concentration. Our alternative approach to controlling the porphyrin–porphyrin interactions in the solid state is to simply incorporate the porphyrin as the core of a dendrimer.

We have previously reported that porphyrin cored dendrimers with stilbene based dendrons attached via phenyl moieties to the meso-positions can be used as neat layers in OLEDs.12,13 We found that the efficiency of the OLEDs was generation-dependent, with the dendrimer having a lower generation generally being more efficient. In this study we have explored the effect of changing the link between core and dendrons on the photophysical and redox properties of the porphyrin core. We have used a stilbene based dendron and compared the properties of the stilbene linked dendrimers with those of phenyl linked dendrimers. The oxidation and reduction half potentials of the two dendrimer families were found to be the same. However, the rate of heterogeneous electron transfer was found to be strongly dependent on link type and generation. The photoluminescence quantum yield (PLQY) of the dendrimers was also found to be strongly dependent on the method of attachment of the core. In solution the dendrimers with the stilbene link between core and dendrons had PLQYs 1.5 times higher than their phenyl counterparts but in the solid state the trend was reversed with the phenyl linked dendrimers generally having a higher PLQY. The difference in properties has been assigned to the comparative openness of the dendrimer architectures and the effect of the dendrons on the shape of the porphyrin core.
dependent with the second generation being twice as efficient as the first. However, the origin of this dependence of efficiency on generation was not clear, that is whether it was due to a difference in luminescence efficiency or charge injection and transport. In this paper we probe the role of the stilbene dendrons in controlling the intermolecular interactions of the porphyrin core both in solution and the solid state using a combination of electrochemistry, photoluminescence and photoluminescence quantum yield measurements. We discuss the effect of generation on the opto-electronic properties of two families of dendrimers that only differ in the way the stilbene dendrons are attached to the porphyrin ring. The first family of dendrimers (1, 2, and 3) have the stilbene dendrons attached to the phenyl ring that is directly connected to the meso-positions of the porphyrin core whilst the second family (15, 16, and 17) has the dendrons connected via the more extended stilbene unit. Finally, we propose an explanation for the observation that OLED efficiency increases with generation.

Results and discussion

Syntheses

The synthesis of the first, 2 ([G-1]PP), and second, 3 ([G-2]PP), generation tetra-phenylporphyrin dendrimers Fig. 1 has been reported previously.6 The strategy for the formation of the tetra-stilbene analogues 15, 16, and 17 is shown in Scheme 1. The basic method involves extending the stilbene dendrons with aldehyde foci, 6, 7, and 8, by the attachment of a 4-styryl benzaldehyde unit before subsequent condensation with pyrrole to give the porphyrin. The extension of the foci was achieved in two steps. The first step involved the reaction of dimethyl 4-cyanobenzylphosphonate 5 with the aldehyde focused dendrons (6–8) to give dendrons with a 4-cyanostyryl focus (9–11). The cyano groups of the 4-cyanostyryl focused dendrons were then reduced with disobutylaluminium hydride (DIBAL-H) and a subsequent aqueous acid hydrolysis gave the aldehyde moiety required for the porphyrin formation. The phosphonate for the Horner–Wadsworth–Emmons reaction was obtained from 4-cyanobenzyl bromide in a yield of 90% after purification by reaction with an excess of trimethyl phosphite at 100 °C.

Following this general procedure the zeroth generation aldehyde 6 was coupled with phosphonate 5 at room temperature using potassium tert-butoxide as base and tetrahydrofuran as solvent. After purification by column chromatography zeroth generation 4-cyanostyryl focused dendron 9 was isolated in an 89% yield. Reduction of 9 with DIBAL-H followed by an aqueous acid work-up gave the 4-styrylbenzaldehyde focused dendron 12 as a mixture of cis- and trans-isomers. This suggests that 9 also contained some cis-isomer. The cis-isomer was equilibrated to the trans-isomer by heating with catalytic iodine in toluene at 100 °C. After purification 12 was isolated in a 95% yield. The first and second generation 4-cyanostyryl focused dendrons 10 and 11 were prepared in an analogous manner to the zeroth generation and were isolated in yields of 92% and 95% respectively. Reduction of nitrile moieties was also carried out under the same conditions as the zeroth generation, but no isomerisation step was required, and after purification by column chromatography the aldehyde 13 was obtained in a yield of 80% and 14 in a yield of 73%.

The final step in the synthesis of the tetra-stilbene porphyrins 15–17 was the trifluoroacetic acid catalysed condensation of the stilbene aldehyde focused dendrons with pyrrole. A solution of the zeroth generation stilbene aldehyde 12 with one equivalent of pyrrole and one equivalent of trifluoroacetic acid in dichloromethane was stirred in the dark under argon for one week to give the zeroth generation tetra-stilbeneporphyrin 15 ([G-0]StP) in a yield of 25% after 2,3-dichloro-5,6-dicyano-1,4-benzoquinone oxidation and purification. The reactions to prepare the first ([G-1]StP) and second ([G-2]StP) generation tetra-stilbeneporphyrin dendrimers 16 and 17 were analogous and after purification the porphyrins were collected in yields of 15% and 22% respectively.

In our previous study of the tetra-phenylporphyrins we found that there was a strong correlation between the hydrodynamic radii and the electrochemical and device properties of the dendrimers. With the extra styryl unit it was expected that the hydrodynamic radii of the tetra-stilbeneporphyrins would be greater than for the tetra-phenylporphyrins. Gel permeation chromatography (GPC) showed that the dendrimers were
mono-disperse and we used $M_v$ along with the Hester–Mitchell equation and the Mark–Houwink relationship to estimate their hydrodynamic radii ($R_h$). The $M_v$ of the [G-0]StP, [G-1]StP, and [G-2]StP generation tetra-stilbeneporphyrins were 2050, 3858, and 6330 respectively corresponding to hydrodynamic radii of 7, 12, and 16 Å for the zeroth to second generation respectively. This corresponds to 43%, 17%, and 19% increases in radii for the equivalent generations. For the tetra-phenylporphyrins it was observed that in moving from the zeroth to second generation there was a dramatic change in the porphyrins’ electrochemical properties. Hence the corresponding increase in radii in going to the tetra-stilbeneporphyrins might also be expected to have a strong effect on the properties of the porphyrin cores.

**Electrochemistry**

We first studied the effect of the introduction of the styryl spacer on the electrochemical properties. The electrochemical properties of the tetra-stilbeneporphyrin dendrimers were studied by cyclic voltammetry and the experiments were carried out under the same conditions used for the tetra-phenylporphyrins so that direct comparison between the two families could be made. The measurements were taken at room temperature as 1.0 mM solutions of the dendrimers in dichloromethane and at a scan rate of 35 mV s$^{-1}$. For all traces the chemical reversibility associated with each electrochemical process was checked by performing repetitious scans. The cyclic voltammograms of [G-0]StP, [G-1]StP, and [G-2]StP are shown in Figs. 2 to 4 and a summary of the results for the tetra-stilbeneporphyrins and tetra-phenylporphyrins are in Table 1. For [G-0]PP three porphyrin based redox processes were observed, two chemically reversible reductions ($-1.76$ and $-2.05$ V) and one chemically reversible oxidation (0.44 V). For the [G-0]StP we again observed two porphyrin based chemically reversible reductions but in contrast to [G-0]PP we also saw two chemically reversible oxidations (Fig. 2). The potentials at which the reductions and first oxidations take place are similar for both porphyrin types. This is consistent with the stilbene units being orthogonal to the porphyrin plane and hence not increasing the conjugation length of the porphyrin core. However, the observation of the chemical reversibility of the porphyrin dication for [G-0]StP indicates that the stilbene unit does have an effect on the oxidative processes. The separation between the anodic ($E_{pa}$) and cathodic ($E_{pc}$) peaks of the first oxidation and reduction of [G-0]StP 15 and [G-0]PP 1 were around 90 mV.

For the first generation tetra-phenylporphyrin [G-1]PP 2 two chemically reversible reductions and one chemically reversible oxidation were also observed. The potentials at which the redox processes occurred were close to those for the zeroth generation. For the [G-1]StP 16 (Fig. 3) the reduction and first oxidation potentials were the same as those for [G-0]StP 15.

**Table 1** Electrochemical data for [G-n]P and [G-n]StP

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>$E_{(1)}$/V</th>
<th>$E_{(2)}$/V</th>
<th>$E_{(1)}$/V</th>
<th>$E_{(2)}$/V</th>
<th>$\Delta E_p$/$\Delta V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+0.44</td>
<td>—</td>
<td>-1.76</td>
<td>-2.08</td>
<td>0.09</td>
</tr>
<tr>
<td>2</td>
<td>+0.56</td>
<td>—</td>
<td>-1.72</td>
<td>-2.04</td>
<td>0.24</td>
</tr>
<tr>
<td>3</td>
<td>—</td>
<td>—</td>
<td>-1.75</td>
<td>-2.17</td>
<td>0.58</td>
</tr>
<tr>
<td>15</td>
<td>+0.45</td>
<td>+0.72</td>
<td>-1.71</td>
<td>-2.02</td>
<td>0.09</td>
</tr>
<tr>
<td>16</td>
<td>+0.47</td>
<td>—</td>
<td>-1.68</td>
<td>-1.98</td>
<td>0.09</td>
</tr>
<tr>
<td>17</td>
<td>+0.54</td>
<td>—</td>
<td>-1.70</td>
<td>-2.03</td>
<td>0.14</td>
</tr>
</tbody>
</table>

$\Delta V_{(1)}$ = first reduction. Conditions: solvent = dichloromethane; [Dendrimer] = 1.0 mM; [(n-Bu)$_4$NPF$_6$] = 0.1 M; glassy carbon working electrode; platinum wire counter electrode; Ag/3 M NaCl/AgCl(sat) reference electrode; ferrocenium/ferrocene couple as standard; scan rate = 35 mV s$^{-1}$. 

![Fig. 2 Cyclic voltammogram of [G-0]StP 15, scan rate = 35 mV s$^{-1}$; potentials are quoted against the ferrocenium/ferrocene couple.](image)

![Fig. 3 Cyclic voltammogram of [G-1]StP 16, scan rate = 35 mV s$^{-1}$; potentials are quoted against the ferrocenium/ferrocene couple.](image)

![Fig. 4 Cyclic voltammogram of [G-2]StP 17, scan rate = 35 mV s$^{-1}$; potentials are quoted against the ferrocenium/ferrocene couple.](image)
However, unlike the zeroth generation only one chemically reversible oxidation was seen for the first generation dendrimer. The second porphyrin based oxidation of the first generation was determined to be close to the potential of a chemically irreversible oxidation, which we believe is due to oxidation of the dendrons. Although the half potentials for the reductions of 2 and 3 are the same there was a distinct difference in the $E_{pa}$ – $E_{pc}$ for the reductions. For the first reduction in going from [G-0]PP 1 to [G-1]PP 2 $E_{pa} – E_{pc}$ increases from 90 mV to 240 mV indicating slowed heterogeneous electron transfer from the electrode to the porphyrin core. This is consistent with an increase in the hydrodynamic radii of the porphyrins. In contrast, in going from the zeroth to first generation in the tetra-stilbeneporphyrin there is no change in $E_{pa} – E_{pc}$ which is $\approx$ 90 mV in both cases. This is in spite of the hydrodynamic radii of [G-1]StP 16 being 40% and 17% larger than that of [G-0]StP 15 and [G-1]PP 2, respectively. This suggests that moving the dendron attachment point further from the core gives a more open flexible structure allowing the porphyrin to be more easily accessed. Interestingly we do not see any hysteresis in the oxidation of [G-1]PP 2 although we do not have an explanation for this at this stage.

Electrochemical analysis of [G-2]PP 3 showed that it had two chemically reversible reductions but no chemically reversible oxidation was observed. For the second generation tetra-stilbeneporphyrin dendrimer [G-2]StP 17 we again observed two chemically reversible reductions and in contrast to [G-2]PP 3 one chemically reversible oxidation (Fig. 4). For [G-2]PP 3 there is a large hysteresis observed for the reduction processes with $E_{pc} – E_{pa} = 580$ mV for the first reduction indicating that the rate of heterogeneous electron transfer is significantly slowed. For [G-2]StP some hysteresis is also observed for the reduction and oxidation processes with the $E_{pc} – E_{pa}$ being $\approx$ 50% greater, at 140–160 mV, than for the first generation. This clearly shows that with the larger dendron the porphyrin core is more shielded although less so than for the tetra-phenylporphyrin dendrimers. This is again consistent with the more open structure caused by the styrene link of the dendron to the porphyrin leaving the porphyrin core more exposed.

It is important to note that the redox potentials at which these processes occurred were the same as those for the lower generations in each of the families indicating that these rigid stilbene dendrons do not create a microenvironment that changes the redox properties of the porphyrins.

Therefore, the electrochemistry indicates that extension of the attachment point of the dendron from a phenyl to a stilbene unit does not change the redox potentials or HOMO–LUMO energy gap of the porphyrin cores. In addition, although the tetra-stilbeneporphyrins have larger hydrodynamic radii than the tetra-phenylporphyrins, the stilbene moiety gives a more open structure causing the porphyrin core to be more accessible.

UV-visible spectra and photoluminescence

The solution UV-visible absorption and photoluminescence (PL) spectra of the tetra-stilbeneporphyrins are shown in Fig. 5. The absorption spectra consist of dendron absorption (PL) spectra of the tetra-stilbeneporphyrins are shown in Fig. 5. The absorption spectra consist of dendron absorption (PL) spectra of the tetra-stilbeneporphyrins which had peaks at 655 and 720 nm. The PL spectra of the three generations of tetra-stilbeneporphyrins show two peaks at 661 and 727 nm corresponding to the Q(0,0) and the Q(0,1) porphyrin core transitions.14 The PL is only slightly red-shifted when compared to the tetra-phenylporphyrin dendrimers which had peaks at 655 and 720 nm. This is consistent with the electrochemical measurements that showed the HOMO–LUMO energy gaps of the two families of materials being essentially the same (Table 1). However, there is a significant difference in the PL spectra between the two families. For the tetra-phenylporphyrin family the weighting of the Q(0,0) and Q(0,1) bands was seen to be generation dependent with the ratio of the Q(0,0) to the Q(0,1) changing from 1 : 0.7 to 1 : 0.9 in going from the zeroth to second generation. The relative intensities of the Q(0,0) and Q(0,1) emission bands is dependent on the relative orbital energies of the excited states of the porphyrins.15,16 Therefore, different ratios of the intensities of the two peaks could imply different porphyrin excited state energies. Such a change has not been reported for porphyrin cored dendrimers with flexible dendrons. We believe that the change in Q(0,0) and Q(0,1) intensities arises from the steric demands of rigid dendrons causing the shape of the porphyrin core to deviate, to different degrees, from planarity. This causes a change to the excited state energy levels which in turn alters the electronic spectra.17 In contrast, no large change is seen in the weighting for the tetra-stilbeneporphyrins and it is only for the second generation that a slight increase in the Q(0,1) compared to the Q(0,0) is observed. In fact it is interesting to note that the Q(0,1) transition for the tetra-stilbeneporphyrins is weaker than for the tetra-phenylporphyrins which would also be consistent with the lower steric demand of the dendrons. That is, the porphyrin ring does not have to change its shape significantly with generation.

In going from solution to the film there is a change in the PL spectra for the tetra-stilbeneporphyrin dendrimers (Fig. 6). For all three generations there is a modest red shift in the peaks, $\approx$ 23 nm for the Q(0,0) and 12 nm for the Q(0,1) transitions, a broadening of the emission, and a pronounced red tail. The broadening of the spectra and red tail suggests the possibility of a contribution to the emission from excimers or aggregates. The contribution to the red end of the spectrum is greatest for the zeroth generation which is consistent with it having the most open structure. The PL spectrum of [G-2]StP is closest to that of the solution spectrum which is also consistent with it
being the most sterically hindered in the series. Another difference between the solution PL and film PL spectra of the tetra-stilbeneporphyrins is that the Q(0,1) transition becomes more pronounced in the solid state. In addition, the ratio of the Q(0,1) to Q(0,0) transitions was found to decrease on going from the zeroeth to first and second generation. We believe one factor causing the change in the ratio of the Q(0,0) to Q(0,1) transitions is that the porphyrin core adopts a different conformation in the solid state with the conformation being partially controlled by the dendrons and solid state intermolecular interactions.

For the more sterically encumbered tetra-phenylporphyrin the changes in the PL spectra are less (Fig. 7). Although there is a red shift in the PL spectra on moving from solution to the solid state it is less than that observed for the tetra-stilbeneporphyrin series with the Q(0,0) and Q(0,1) peaks moving to the red by only \( \approx 14 \) nm and \( \approx 8 \) nm respectively. The PL spectra are only slightly broader in the solid state in marked contrast to the tetra-stilbeneporphyrin family. However, the largest difference between the solution and solid state PL spectra is in the weighting of the Q(0,0) and Q(0,1) transitions. In solution we observed that the ratio of these transitions increased with increasing generation. However, in the solid state this trend is reversed with the Q(0,1) being the main transition for the zeroeth generation dendrimer with it decreasing with increasing generation. For the second generation the ratio of the Q(0,0) to Q(0,1) transitions in the solid state was seen to begin to reach parity with the solution spectrum. These PL spectra again clearly demonstrate that the porphyrin emission is very sensitive to the porphyrin shape, which can be governed by the local environment which in turn can be controlled by the method of dendron attachment and generation. It is interesting to note that even the zeroeth generation of the tetra-phenylporphyrin series has less of a red tail. We believe this is due to the bulky tert-butyl groups being attached close enough to the porphyrin core to decrease the level of porphyrin π-stacking. This view is consistent with the physical properties of [G-0]PP which is far more soluble than the simple meso-tetraphenylporphyrin which lacks the bulky groups. Therefore, the branching of the stilbene dendrons closer to the core gives better control of the core-core interactions.

The different abilities of the phenyl and stilbenyl attachment to the porphyrin ring to control the core-core interactions was confirmed by PL quantum yield (PLQY) measurements. We carried out the measurements in both solution and the solid state and the results are summarised in Table 2. For the tetra-phenylporphyrin dendrimers the solution PLQYs were found to be independent of generation and around 10–12%. With the attachment of the dendrons via the stilbene rather than a phenyl unit the PLQY was seen to increase by around 50% and were found to be similar for all generations. That is, the attachment of the dendrons via stilbene units enhances the PLQY of the porphyrins. However, in going from solution to the solid state we observe the most interesting PLQY results. It might be expected that for the zeroeth generation dendrimers in each family we might see a decrease in the film PLQY due to π-stacking but observe a significant increase in going to higher generations as the core becomes more protected by the dendrons. However, this is not the case for either family. For the tetra-phenylporphyrin dendrimer family there is a five-fold decrease in going from solution to the solid state with all generations essentially having the same PLQY. For the tetra-stilbeneporphyrins the decrease in PLQY is approximately eighteen-fold for the zeroeth and first generation and ten-fold for the second generation. The decrease in PLQY of almost an order of magnitude seen for both families of dendrimers in going from solution to the solid state indicates that there is enhanced non-radiative decay in the solid state. Enhanced non-radiative decay can arise from the migration of excited states to quenching sites including excimers and aggregates. This larger relative decrease for the tetra-stilbeneporphyrins is consistent with them having a more open structure allowing increased porphyrin core-core interactions.

A final aspect of this paper is an understanding of the improvement in OLED performance in going from the first to second generation in the tetra-phenylporphyrin series. The electroluminescence external quantum efficiency for the first generation was 0.02% and for the second 0.04% in a device configuration of ITO/molecular fluorescent material/Ca. Although these EL efficiencies are not very high they actually do represent almost optimised efficiency for these fluorescent materials. Given that OLEDs based on molecular fluorescent materials can only have a maximum internal efficiency of 25% of the PLQY the maximum internal EL efficiency of [G-1]PP and [G-2]PP based devices can only be of the order 0.45%. However, the outcoupling of light in these simple devices is usually around a fifth due to the refractive indices of the materials. This means that the maximum external efficiency of devices based on these two porphyrins would be around 0.09%. Therefore, given that the PLQY of the two dendrimers is the same we believe that the difference in efficiency is likely to be due to the difference in charge mobility, which is governed by generation.

**Conclusion**

We have found in a new family of porphyrin core conjugated dendrimers with stilbene based dendrons that the proximity of the first branching point is important in controlling the core-core interactions. We have shown that when the dendrons are attached via a stilbene unit the dendrimer is more open and the cores more susceptible to intermolecular interactions than when the dendrons are connected via a phenyl ring. Whilst the dendrimers with the stilbene links between the dendrons and the porphyrin core show superior electrochemical and photo-luminescence properties in solution, in the solid state the
phenyl linked dendrimers were more luminescent. Therefore, when designing conjugated dendrimers it is necessary not only to choose the correct type of dendron for the core but also the correct linking unit between dendron and core.

**Experimental**

**Measurements**

NMR spectra were recorded on a Bruker DPX 400 MHz or an AMX 500 MHz spectrometer; \(s_p = \) surface phenyl; \(c_p = \) core phenyl; \(c_v = \) core vinyl; \(b_p = \) branch phenyl. All \(J\) values are in Hertz. IR spectra were recorded on a Perkin-Elmer 1000 infrared spectrometer. UV-visible spectra were recorded on a Perkin-Elmer UV-visible Lambda 14P spectrometer and were recorded as a solution in spectroscopic grade chloroform, dichloromethane, or methanol. Mass spectra were recorded on a Hewlett-Packard 1050 atmospheric pressure chemical ionisation mass spectrometer (APCI) (+ve mode) or a Micromass TofSpec 2E for matrix-assisted laser desorption/ ionisation–time-of-flight (MALDI-TOF) from dithranol (1,8,9-trihydroxyanthracene) in reflectron mode. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Microanalyses were carried out in the Inorganic Chemistry Laboratory, Oxford, UK. Gel permeation chromatography was carried out using PLgel Mixed-A columns (600 mm x 300 mm lengths, 7.5 mm diameter) fromPolymer Laboratories calibrated with polystyrene narrow molecular weight standards (MP = 1300 to 11.2 \(\times 10^3\)) in tetrahydrofuran with toluene as flow marker. The tetrahydrofuran was degassed and the sphere was purged with nitrogen. ¡

When solvent mixtures are used for chromatography over silica, Light petroleum refers to the fraction of boiling point 60–90 °C.

These measurements is estimated to be \(15\%\) of the stated value. When designing conjugated dendrimers it is necessary not only to choose the correct type of dendron for the core but also the correct linking unit between dendron and core.

(4-Cyanobenzyl)phosphonic acid dimethyl ester 5

A suspension of 4-(bromomethyl)benzonitrile (27.9 g, 0.142 mmol) in trimethyl phosphite (84.0 cm³, 0.711 mmol) was stirred at 100 °C for 66 h. Unreacted trimethyl phosphite was removed by distillation under reduced pressure. The residue was purified by column chromatography over silica using a dichloromethane–ethyl acetate mixture (1 : 1) as eluent, to give a white solid of 5 (28.9 g, 90%). The 2,3-di-(tert-butyl)phenyl derivative of 5 was used as the reference material.規模は horn。The 2,3-di-(tert-butyl)phenyl derivative of 5 was used as the reference material.規模は horn。
A solution of 12 (2.00 g, 6.24 mmol), pyrrole (0.43 g, 6.2 mmol) and trifluoroacetic acid (0.480 ml, 6.24 mmol) in dichloromethane (460 cm$^3$) was stirred in the dark under argon for 7 days. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (1.42 g, 6.24 mmol) was added and the mixture stirred for 10 min. The solution was neutralised by the addition of an excess of sodium hydrogen carbonate then filtered through a plug of silica using a dichloromethane–light petroleum mixture (1 : 2 to 1 : 0) as eluent. The main fraction was collected, the solvent removed, and the residue recrystallised from a dichloromethane–methanol mixture to give 15 (563 mg, 25%) as a red-purple solid. Mp > 270 °C (decomp.) (Found: C, 89.0; H, 8.8; N, 2.2%).

**[G-1]SIP 15**

A solution of 13 (1.00 g, 1.57 mmol), pyrrole (157 ml, 2.26 mmol) and trifluoroacetic acid (121 ml, 1.57 mmol) in dichloromethane (114 cm$^3$) was stirred at room temperature under argon for 9 days. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (357 mg, 1.57 mmol) was added and the mixture stirred for 30 min. The solution was neutralised by the addition of an excess of sodium hydrogen carbonate then filtered through a short plug of silica using dichloromethane as eluent. The main fraction was collected, the solvent removed and the residue recrystallised from a dichloromethane–methanol mixture to give a red-purple solid of 16 (153 mg, 15%). Mp > 279 °C (decomp.) (Found: C, 89.1; H, 8.2; N, 2.2. C$_{30}$H$_{32}$N$_4$ requires C, 89.5; H, 8.5; N, 2.1%).

**[G-1]SIP 16**

A solution of 17 (0.467 g, 2.44 mmol) in dichloromethane (25 cm$^3$) was stirred at room temperature for 20 min, added and the mixture stirred for 30 min. The solution was neutralised by the addition of an excess of sodium hydrogen carbonate then filtered through a short plug of silica using dichloromethane as eluent. The main fraction was collected, the solvent removed and the residue recrystallised from a dichloromethane–methanol mixture to give a red-purple solid of 18 (74.3 mg, 13%). Mp > 252 °C (decomp.) (Found: C, 89.0; H, 8.8; N, 2.2%).
eluent to give a white solid of 14 (2.31 g, 73%). Mp > 250 °C (Found: C, 89.8; H, 8.9. C37H41Cl2O requires C, 90.2; H, 8.9%).

A mixture of [G-2]StP 17 (4.38), 559 (4.35), 595 (3.88) and 651 (3.94); δHmax (CDCl3) 7.46 (8 H, d, J16, cv H), 7.46 (8 H, d, J16, G2-vinyl H), 7.30 and 7.37 (2 H, d, J16, G2-vinyl H), 7.33 (4 H, s, G1 vinyl H), 7.38 (4 H, dd, J2 and 2, sp H), 7.46 (8 H, d, J2, sp H), 7.68 (8 H, m, G1-bp H and G2-bp H), 7.75 and 7.94 (4 H, AA'BB', cp H), 7.76 (1 H, br m, G1-bp H) and 10.05 (1 H, s, CHO); m/z (MALDI) 1269.9 (M⁺, 100%).

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References