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

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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 phenylene^{7,8} 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 π -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



Fig. 1 Porphyrin cored dendrimers with stilbene dendrons linked to the core via phenyl units.

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 cores 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-styrylbenzaldehyde 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 diisobutylaluminium 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 4 in a yield of 90% after purification by reaction with an excess of trimethyl phosphite at 100 °C.

Following this general procedure the zeroeth 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 zeroeth 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 transisomers. 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 zeroeth 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 zeroeth 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-stilbeneporphyrins **15–17** was the trifluoroacetic acid catalysed condensation of the stilbene aldehyde focused dendrons with pyrrole. A solution of the zeroeth 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 zeroeth 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



Scheme 1 Reagents and conditions: i, $P(OMe)_3$, $100 \,^{\circ}C$; ii, *t*-BuOK, THF, rt; iii, DIBAL-H, THF, $-78 \,^{\circ}C$, then $HCl_{(aq)}$, rt; iv, pyrrole, CF₃CO₂H, CH₂Cl₂, Ar, rt then DDQ.

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 $\bar{M}_{\rm v}$ along with the Hester–Mitchell equation and the Mark-Houwink relationship to estimate their hydrodynamic radii (R_h) .¹³ The \overline{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 10, 14, and 19 Å respectively. These radii are larger than those of the tetra-phenylporphyrin derivatives which had radii of 7, 12, and 16 Å for the zeroeth to second generation respectively.¹³ 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 zeroeth to second generation there was a dramatic change in the porphyrins' electrochemical properties. Hence the corresponding increase in radii in going to the tetrastilbeneporphyrins 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 tetraphenylporphyrins 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



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



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



Fig. 4 Cyclic voltammogram of [G-2]StP 17, scan rate = 35 mV s⁻¹; potentials are quoted against the ferrocenium/ferrocene couple.

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 zeroeth 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

Dendrimer	<i>E</i> (o1)/V	<i>E</i> (o2)/V	<i>E</i> (r1)/V	<i>E</i> (r2)/V	$\Delta E_{\rm p}({\rm r1})^a/{\rm V}$
1	+0.44		-1.76	-2.08	0.09
2	+0.56		-1.72	-2.04	0.24
3			-1.75	-2.17	0.58
15	+0.45	+0.72	-1.71	-2.02	0.09
16	+0.47		-1.68	-1.98	0.09
17	+0.54		-1.70	-2.03	0.14
<i>a</i>		~			

 a rl = first reduction. Conditions: solvent = dichloromethane; [Dendrimer] = 1.0 mM; [(*n*-Bu)₄NPF₆] = 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.

However, unlike the zeroeth 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 16 are the same there was a distinct difference in the $E_{\rm pa}$ $-E_{\rm pc}$ 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 zeroeth to first generation in the tetra-stilbene
porphyrin there is no change in $E_{\rm pa}-E_{\rm pc}$ 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 tetrastilbeneporphyrin 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 $E_{\rm pa} - E_{\rm pc} = 580$ 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 $E_{\rm pa}$ – $E_{\rm pc}$ 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 tetraphenylporphyrin 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 with a peak around 310 nm, which increases in intensity with increasing generation number, the porphyrin Sorét band at 430 nm and four porphyrin Q bands between 520 and 655 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



Fig. 5 Solution UV-vis and PL spectra for 15, 16, and 17.

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 zeroeth 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, ≈ 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 zeroeth 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



Fig. 6 Film PL spectra for 15, 16, and 17.



Fig. 7 Film PL spectra for 1, 2, and 3.

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 tetrastilbeneporphyrin series with the Q(0,0) and Q(0,1) peaks moving to the red by only ≈ 14 nm and ≈ 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 tetraphenylporphyrin 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

Table 2 Dendrimer PLQYs

Dendrimer	$\lambda_{\rm ex}/{\rm nm}$ (solution)	$\operatorname{PLQY}_{\mathrm{sol}}_{(\%)^a}$	PLQY _{film} (%)	Film thickness/nm	Film abs. (<i>a</i>) λ_{ex}
1	419	12	2.2^{b}	130	0.4
2	429	12	1.7^{b}	110	0.9
3	429	10	1.8^{b}	130	0.4
15	427	15	0.81^{c}	130	0.65
16	427	18	0.98^{c}	150	1.0
17	428	17	1.9 ^c	160	0.5
a A 11 1 1				1 1 0	

^aAll solution measurements were taken in tetrahydrofuran (HPLC grade). ^bFilm spun from tetrahydrofuran. ^cFilm spun from chloroform. Films excited at 442 nm.

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.¹⁸ However, this is not the case for either family. For the tetra-phenylporphyrin dendrimer family there is a fivefold decrease in going from solution to the solid state with all generations essentially having the same PLQY. For the tetrastilbeneporphyrins 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 nonradiative 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-porphyrin 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/porphyrin/Ca.12 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 cored conjugated dendrimers with stilbene based dendrons that the proximity of the first branching point is important in controlling the corecore 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 photoluminescence 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: sp = surface phenyl; cp = corephenyl; cv = core vinyl; bp = 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 (1,8,9trihydroxyanthracene) 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 µm Mixed-A columns (600 mm + 300 mm lengths, 7.5 mm diameter) from Polymer Laboratories calibrated with polystyrene narrow standards (Mp = 1300 to 11.2×10^6) in tetrahydrofuran with toluene as flow marker. The tetrahydrofuran was degassed with helium and pumped at a rate of 1 mL min⁻¹ at 30.0 °C. Light petroleum refers to the fraction of boiling point 60-80 °C, unless otherwise stated, and ether refers to diethyl ether. When solvent mixtures are used for chromatography over silica the proportions are given by volume.

Electrochemistry was performed using an EG&G Princeton Applied Research potentiostat/galvanostat model 263A. All measurements were made at room temperature on samples dissolved in freshly distilled dichloromethane with 0.1 M tetran-butylammonium hexafluorophosphate as the electrolyte. Dichloromethane was purified by the literature procedure and then freshly distilled from calcium hydride.¹⁹ The electrolyte was purified by recrystallisation from ethanol. The solutions were deoxygenated with argon. A glassy carbon working electrode, platinum wire counter electrode, and Ag/3 M NaCl/ AgCl(sat) reference electrode were used. The ferrocenium/ ferrocene couple was used as standard,²⁰ and the ferrocene was purified by sublimation. Figs. 2-4 show a small chemically reversible process near 0 V due to residual ferrocene. In all cases several scans were carried out to confirm the chemical reversibility of the redox processes.

Solution photoluminescence quantum yields (PLQYs) were measured by a relative method using rhodamine 101 in ethanol at room temperature as a standard.²¹ The dendrimers were dissolved in tetrahydrofuran (THF) and freeze-thaw degassed. Photoluminescence spectra were recorded in a JY Horiba Fluoromax 2 fluorimeter, with the dendrimer solutions excited at the Sorét maxima. The absorbances of the standard and samples were similar and small (≤ 0.1). The accuracy of these measurements is estimated to be $\pm 15\%$ of the stated value.

Films were spin-coated from a THF or chloroform solution with a dendrimer concentration of 10 mg ml⁻¹ at 1000 rpm for 1 min to give a thickness of about 150 nm. Their PLQYs were measured using an integrating sphere in accordance with Greenham *et al.*²² using a Helium Cadmium laser (Kimmon) as the excitation source. The excitation power was 0.05 mW at 442 nm and the sphere was purged with nitrogen.

(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 : 0 to 0 : 1) as eluent, to give a white solid of **5** (28.9 g, 90%). Mp 80-81 °C (Found: C, 53.3; H, 5.4; N, 6.25. C₁₀H₁₂NO₃P requires C, 53.3; H, 5.4; N, 6.2%); v_{max} (KBr)/cm⁻¹ 2225 (C=N), 1254 (P=O) and 1054 and 1035 (P–O–C); λ_{max} (MeOH)/nm 233 [log *a*/dm³ mol⁻¹ cm⁻¹ (4.27)], 239sh (4.21), 263sh (2.75), 271 (2.85) and 281 (2.80); δ_{H} (400 MHz, CDCl₃) 3.19 (2 H, d, *J* 22, CH₂P), 3.68 (6 H, d, *J* 11, OCH₃) and 7.39 and 7.59 (4 H, AA'BB'); δ_{C} (100.6 MHz, CDCl₃) 33.1 (d, *J* 138, CH₂P), 53.0 (d, *J* 7, CH₃), 111.0 (d, *J* 4), 118.6 (d, *J* 2), 130.5 (d, *J* 6), 132.3 (d, *J* 3) and 137.1 (d, *J* 10); *m/z* (APCI⁺) 226.1 (MH⁺, 100%).

(*E*)-4-[2-(3,5-Di-*tert*-butylphenyl)vinyl]benzonitrile: [G-0]StCN 9

Potassium *tert*-butoxide (5.92 g, 52.7 mmol) was added to a stirred solution of 3,5-di-*tert*-butylbenzaldehyde **6** (9.599 g, 43.96 mmol) and **5** (10.0 g, 52.7 mmol) in tetrahydrofuran (100 cm³). The reaction was initially exothermic and the solution was stirred at room temperature for 19 h. Water (250 cm³) was added and the aqueous layer was separated and extracted with ether (100 cm³). The organic layers were combined and washed with brine (100 cm³), dried over anhydrous magnesium sulfate, filtered and the solvent removed. The residue was purified by column chromatography over silica using a dichloromethane–light petroleum mixture (2 : 3) as eluent to give **9** as a white solid (12.5 g, 89%), mp 145 °C (lit. 146.5 °C²³).

(*E*)-4-[2-(3,5-Di-*tert*-butylphenyl)vinyl]benzaldehyde: [G-0]StCHO 12

A solution of 9 (10.0 g, 31.5 mmol) in toluene (50 cm³) and dichloromethane (50 cm³) was cooled to -78 °C. Diisobutylaluminium hydride (1.0 M in hexanes, 45 cm³, 45 mmol) was added and the solution stirred at -78°C for 30 min then at room temperature for 19 h. Aqueous hydrochloric acid (3 M, 100 cm³) was added and the mixture stirred for 3 min. The solution was extracted with ether (250 cm^3) and the extract was washed with aqueous hydrochloric acid (3 M, 100 cm³), water (100 cm³), aqueous sodium bicarbonate (5% w/v, 100 cm³), brine (100 cm³), dried over anhydrous magnesium sulfate, filtered and the solvent removed. The residue was dissolved in toluene (100 cm³) and heated with catalytic iodine (400 mg, 1.58 mmol) under argon at 100 °C for 24 h and allowed to cool. The solution was washed with saturated sodium metabisulfite $(2 \times 100 \text{ cm}^3)$ and brine (100 cm³), dried over anhydrous magnesium sulfate, filtered and the solvent removed. The residue was purified by passing through a plug of silica with a dichloromethane-light petroleum mixture (1 : 1) as eluent to give a pale yellow solid of 12 (4.95 g, 95%). Mp 93-94 °C (Found: C, 86.2; H, 8.8. $C_{23}H_{28}O$ requires C, 86.2; H, 8.8%); $v_{max}(KBr)/cm^{-1}$ 1695 (C=O), 1599 (C=C) and 969 (C=C-H *trans*); λ_{max} (CHCl₃)/nm 342 [log ε /dm³ mol⁻¹ cm⁻¹ (4.53)]; δ_{H} (400 MHz, CDCl₃) 1.39 (18 H, s, t-butyl H), 7.16 and 7.33 (2 H, d, J 16, vinylic H), 7.43 (3 H, m, sp H), 7.69 and 7.88 (4 H, AA'BB', cp H) and 10.01(1 H, s, CHO); δ_c(100.6 MHz, CDCl₃) 31.4, 34.9, 121.2, 123.0, 126.6, 126. 8, 130.2, 133.4, 135.1, 135.7, 143.8, 151.2 and 191.6; *m*/*z* (APCI+) 321.3 (MH⁺, 100%).

[G-0]StP 15

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 cm³) 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 dichloromethanemethanol mixture to give 15 (563 mg, 25%) as a red-purple solid. Mp > 280 °C (decomp.) (Found: C, 87.45; H, 7.9; N, 3.85. C₁₀₈H₁₁₈N₄ requires C, 88.1; H, 8.1; N, 3.8%); v_{max}(KBr)/ cm⁻¹ 3320 (N–H) and 964 (C=C–H *trans*); λ_{max} (CH₂Cl₂)/nm 305 [log ε /dm³ mol⁻¹ cm⁻¹ (5.01)], 429 (5.85), 521 (4.31), 559 (4.28), 594 (3.84) ad 652 (3.93); $\delta_{\rm H}$ (500 MHz, CDCl₃) -2.68 (2 H, s, NH), 1.45 (72 H, s, t-butyl), 7.45 and 7.51 (8 H, d, J 16, cv H), 7.46 (4 H, dd, J 1.5 and 1.5, sp H), 7.55 (8 H, d, J 1.5, sp H), 7.95 and 8.25 (16 H, AA'BB', cp H) and 8.97 (8 H, s, β-pyrrolic H); m/z (MALDI) calc. 1471.9; found 1471.9 (M⁺) 100%).

[G-1]StCN 10

Potassium tert-butoxide (1.01 g, 9.00 mmol) was added to a stirred solution of 7 (4.00 g, 7.38 mmol) and 5 (2.02 g, 8.97 mmol) in tetrahydrofuran (80 cm³), and the mixture stirred at room temperature for 16.5 h. Water (100 cm³) was added and the resultant slurry extracted with dichloromethane $(1 \times 200 \text{ cm}^3, 1 \times 100 \text{ cm}^3)$. The organic layers were combined and washed with brine (100 cm³), dried over anhydrous magnesium sulfate, filtered and the solvent removed. The residue was purified by column chromatography over silica using a dichloromethane-light petroleum mixture (2 : 3) as eluent to give a white solid of 10 (4.36 g, 92%). Mp 254-255 °C (Found: C, 89.0; H, 8.8; N, 2.2. C₄₇H₅₅N requires C, 89.05; H, 8.7; N, 2.2%); v_{max}(KBr)/cm⁻¹ 2223 (C=N) and 959 (C=C-H *trans*); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 322 [log $\varepsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (4.93)], 332sh (4.89); $\delta_{\rm H}$ (400 MHz, CDCl₃) 1.39 (36 H, s, *t*-butyl H), 7.17 and 7.28 (4 H, d, J 16, G1-vinyl H), 7.22 and 7.29 (2 H, d, J 16, cv H), 7.40 (2 H, dd, J 1.5 and 1.5, sp H), 7.43 (4 H, d, J 1.5, sp H), 7.60 (2 H, d, J 1, G1-bp H), 7.64 (2 H, 1/2AA'BB', cp H) and 7.67-7.69 (3 H, m, cp H and G1-bp H); m/z (APCI+) 634.5 (MH⁺, 15%).

[G-1]StCHO 13

A solution of 10 (4.00 g, 6.31 mmol) in dichloromethane (25 cm³) and toluene (25 cm³) was cooled to -78 °C under argon. Diisobutylaluminium hydride (1.0 M in hexanes, 8.8 cm³, 8.8 mmol) was added and the mixture was stirred at -78 °C for 30 min. The reaction mixture was then allowed to warm to room temperature and stirred for 19.5 h. Aqueous hydrochloric acid (3 M, 80 cm³) was added carefully and the mixture stirred for 30 min, then extracted with dichloromethane (2 \times 80 cm³). The organic layers were combined, washed with aqueous hydrochloric acid (3 M, 100 cm³) and brine (100 cm³), dried over anhydrous magnesium sulfate, filtered and the solvent removed. The residue was purified by column chromatography over silica using a dichloromethanelight petroleum mixture (1:1) as eluent to give a white solid of 13 (3.23 g, 80%). Mp 235 °C (Found: C, 88.6; H, 8.8. C₄₇H₅₆O requires C, 88.6; H, 8.9%); v_{max}(KBr)/cm⁻¹ 1688 (C=O) and 954 (C=C-H *trans*); λ_{max} (CH₂Cl₂)/nm 323 [log ε /dm³ mol⁻¹ cm⁻¹ (5.32)], 331sh (5.29) and 358sh (5.03); $\delta_{\rm H}(400 \text{ MHz}, \text{CDCl}_3)$ 1.40 (36 H, s, t-butyl H), 7.18 and 7.29 (4 H, d, J 16, G1vinyl H), 7.28 and 7.35 (2 H, d, J 16, cv H), 7.41 (2 H, dd, J 1.5 and 1.5, sp H), 7.44 (4 H, d, J 1.5, sp H), 7.63 (2 H, s, G1-bp H),

7.68 (1 H, s, G1-bp H), 7.72 and 7.91 (4 H, AA'BB', cp H) and 10.03 (1 H, s, CHO); m/z (APCI+) 637.5 (MH⁺, 100%).

[G-1]StP 16

A solution of 13 (1.00 g, 1.57 mmol), pyrrole (157 $\mu l,$ 2.26 mmol) and trifluoroacetic acid (121 µl, 1.57 mmol) in dichloromethane (114 cm³) 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 and the solvent removed. The residue was purified by column chromatography over silica using a dichloromethane-light petroleum mixture (1 : 3 to 2 : 3) 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. $C_{204}H_{230}N_4$ requires C, 89.5; H, 8.5; N, 2.1%); $\nu_{max}(KBr)/cm^{-1}$ 3317 (N–H), 1594 (C=C) and 961 (C=C–H *trans*); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 318 [log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (4.60)], 335sh (4.45), 429 (4.85), 444 (2.88), 521 (3.41), 559 (3.38), 595 (2.94) and 652 (2.99); $\delta_{\rm H}(500 \text{ MHz}, \text{CDCl}_3) - 2.65$ (2 H, s, NH), 1.41 (144 H, s, t-butyl), 7.25 and 7.36 (16 H, d, J 16, G1vinyl H), 7.41 (8 H, dd, J 1.5 and 1.5, sp H), 7.48 (16 H, d, J 1.5, sp H), 7.51 and 7.60 (4 H, d, J 16, cv H), 7.72 (4 H, s, G1-bp H), 7.76 (8 H, s, G1-bp H), 7.99 and 8.29 (16 H, AA'BB', cp H) and 8.99 (8 H, s, β-pyrrolic H); *m*/*z* (MALDI) 2738.4 (M⁺, 100%).

[G-2]StCN 11

Potassium tert-butoxide (0.50 g, 4.45 mmol) was added to a stirred suspension of 8 (4.00 g, 3.42 mmol) and 5 (1.00 g, 4.45 mmol) in tetrahydrofuran (100 cm³) and the reaction mixture was stirred at room temperature for 67 h under argon. Water (100 cm³) was added and the mixture extracted with dichloromethane (1 \times 200 cm³, 1 \times 100 cm³). The organic layers were combined, washed with water (100 cm³) and brine (100 cm³), dried over anhydrous magnesium sulfate, filtered and the solvent removed. The residue was purified by column chromatography over silica using a dichloromethane-light petroleum mixture (1 : 1) as eluent followed by recrystallisation from a dichloromethane-light petroleum mixture to give a white solid of 11 (4.11 g, 95%). Mp > 290 °C (decomp.) (Found: C, 90.1; H, 8.8; N, 1.1. C₉₅H₁₁₁N requires C, 90.1; H, 8.8; N, 1.1%); v_{max}(KBr)/cm⁻¹ 2226 (C=N), 1595 (C=C) and 960 (C=C-H *trans*); λ_{max} (CH₂Cl₂)/nm 323 ([log(ε /dm³ mol⁻¹ cm⁻¹) 5.27] and 332sh (5.23); $\delta_{\rm H}$ (400 MHz, CDCl₃) 1.41 (72 H, s, t-butyl), 7.20 and 7.31 (8 H, d, J 16, G2-vinyl H), 7.24 and 7.31 (2 H, m, cv H), 7.32 (4 H, s, G1-vinyl H), 7.41 (4 H, dd, J 1.5 and 1.5, sp H), 7.46 (8 H, d, J 1.5, sp H), 7.66-7.72 (10 H, m, G1-bp H, G2-bp H, and cp H), 7.70 (2 H, 1/2AA'BB', cp H) and 7.76 (1 H, br m, G1-bp H); *m*/*z* (MALDI) 1266.9 (M⁺, 100%).

[G-2]StCHO 14

A suspension of 11 (3.17 g, 2.50 mmol) in dichloromethane (25 cm³) and toluene (23 cm³) was stirred at -78 °C under argon. Diisobutylaluminium hydride (1.5 M in toluene, 2.20 cm³, 3.25 mmol) was added and the mixture stirred at -78 °C for 10 min and allowed to warm to room temperature, with stirring, over 20.5 h. Aqueous hydrochloric acid (3 M, 20 cm³) was carefully added and the mixture stirred for 20 min, then extracted with dichloromethane (2 × 100 cm³). The organic layers were combined, washed with water (100 cm³) and brine (100 cm³), dried over anhydrous magnesium sulfate, filtered and the solvent removed. The residue was purified by column chromatography over silica with dichloromethane as

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eluent to give a white solid of **14** (2.31 g, 73%). Mp > 250 °C (Found: C, 89.8; H, 8.9. C₉₅H₁₁₂O requires C, 90.0; H, 8.9%); v_{max} (KBr)/cm⁻¹ 1697 (C=O), 1597 (C=C) and 960 (C=C-H *trans*); λ_{max} (CH₂Cl₂)/nm 323 [log ε /dm³ mol⁻¹ cm⁻¹ (5.36)] and 333sh (5.32); δ_{H} (400 MHz, CDCl₃) 1.41 (72 H, s, *t*-butyl), 7.21 and 7.32 (8 H, d, *J* 16, G2-vinyl H), 7.30 and 7.37 (2 H, d, *J* 16, cv H), 7.33 (4 H, s, G1 vinyl H), 7.38 (4 H, dd, *J* 2 and 2, sp H), 7.46 (8 H, d, *J* 2, 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%).

[G-2]StP 17

A mixture of 14 (1.000 g, 0.787 mmol), pyrrole (55.0 µl, 0.787 mmol), and trifluoroacetic acid (90.0 mg, 0.787 mmol) in dichloromethane (60.0 cm³) was stirred at room temperature under argon for 12 days. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (393 mg, 1.96 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, eluting with dichloromethane. The solvent was removed and the residue was purified by column chromatography over silica using a dichloromethanelight petroleum mixture (1 : 4 to 2 : 3) as eluent. The main fraction was collected, the solvent removed and the residue recrystallised from a dichloromethane-methanol mixture to give 17 (232 mg, 22%) as a red-purple solid. Mp 286 °C (decomp.) (Found: C, 89.7; H, 8.7; N, 1.3. C₃₉₆H₄₅₄N₄ requires C, 90.25; H, 8.7; N, 1.1%); v_{max} (KBr)/cm⁻¹ 1594 (C=C) and 960 (C=C–H *trans*); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 314sh (log ($\varepsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 5.92), 322 (5.94), 331sh (5.86), 430 (5.85), 488sh (3.91), 521 (4.38), 559 (4.35), 595 (3.88) and 651 (3.94); $\delta_{\rm H}$ (500 MHz, CDCl₃) -2.62 (2 H, s, NH), 1.40 (288 H, s, t-butyl), 7.22 and 7.33 (32 H, d, J 16, G2 vinyl H), 7.39-7.40 (32 H, G1 vinyl H and sp H), 7.46 (32 H, d, J 1.5, sp H), 7.56 and 7.63 (8 H, d, J 16, cv H), 7.68 (8 H, s, G2-bp H), 7.71 (16 H, s, G2-bp H), 7.80 (4 H, s, G1-bp H), 7.82 (8 H, s, G1-bp H), 8.03 and 8.32 (16 H, AA'BB', cp H) and 9.02 (8 H, s, β-pyrrolic H); m/z (MALDI) 5272.6 (M⁺, 100%).

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