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A Facile Iterative Procedure for the Preparation of Dendrimers Containing Luminescent Cores and Stilbene Dendrons

Jonathan N. G. Pillow,[†] Mounir Halim,[‡] John M. Lupton,[‡] Paul L. Burn,*[,†] and Ifor D. W. Samuel*[,‡]

The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QY, U.K., and Department of Physics, University of Durham, South Road, Durham DH1 3LE, U.K.

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ABSTRACT: A simple two-step convergent iterative procedure has been developed for the preparation of stilbene dendrons containing an aldehyde at the center which can be coupled in a single step to give dendrimers that contain luminescent chromophores. The stilbene units in the dendrons are linked in a *meta* arrangement at the branching phenyl units allowing them to be treated, to a first approximation, as isolated chromophores. All the dendrimers are luminescent with emission observed from the core. The cores prepared were distyrylbenzene, distyrylanthracene, and *meso*-tetraphenylporphyrin which photoluminesce blue, yellow-green, and red, respectively. We found that all the dendrimers, independent of generation or core, could be spin-coated from solution to form good quality thin films, which shows that the processing conditions have been disengaged from the electronic properties in this series of materials.

Introduction

The interest in conjugated organic materials has undergone an extended renaissance since the discovery that conjugated polymers could be used as the light-emitting layer in light-emitting diodes.[1] The field of light-emitting materials has until recently been divided into molecular materials,[2] which are generally deposited by evaporation, and polymers, which are often deposited by spin-coating from solution.[3] One issue that affects both polymers[4] and molecular materials is that changes in the molecular structure to effect a variation in the electronic properties can often change the physical and hence processing properties of the material. Dendritic structures, on the other hand, offer a unique opportunity to vary the physical and electronic properties independently. The ability to independently vary the physical and electronic properties arises from the fact that in higher dendrimer generations it is only the surface groups which are in contact with the environment. The synthetic strategies for the formation of dendrimers are now well understood.[5] Of the two main strategies, convergent and divergent, the former is preferred as it limits the number of reactions that are carried out at each iterative step for the formation of the next generation. Much of the early interest in dendrimers was on understanding the effect of generation on the physical properties. However, more recently, dendrimers which contain electroactive organic moieties have been developed.[6] Of particular interest to our work is the fact that dendrimers have been used as the charge transport layers in light-emitting diodes (LEDs), and more recently there have been a few reports of dendrimers being used as the light-emitting layer in LEDs.[6a,h,7] For organic materials to be used successfully as the light-emitting layer in LEDs, there must be efficient and balanced charge injection from the two electrodes, good charge mobility through the device, and efficient singlet exciton formation and decay. For good charge mobility, it is necessary to keep the insulating component of the light-emitting material to a minimum, and therefore, dendrimers which consist of luminescent cores but insulating dendrons such as those based on benzyl ethers[2g,8] or alkylamide and ether links[6c] will be potentially of less use than if the dendrons consist of conjugated units. We were therefore interested in developing luminescent dendrimers which have conjugated moieties in the dendrons, for

[†] University of Oxford.
[‡] University of Durham.

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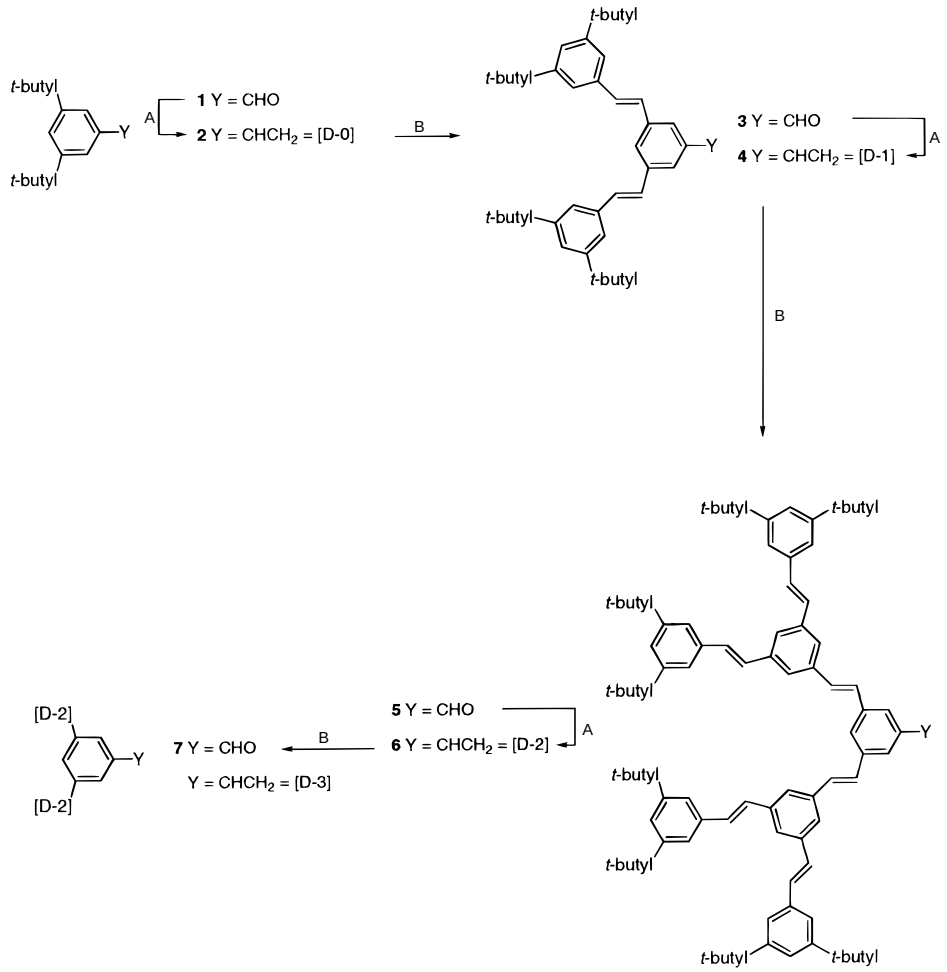
Scheme 1[a]



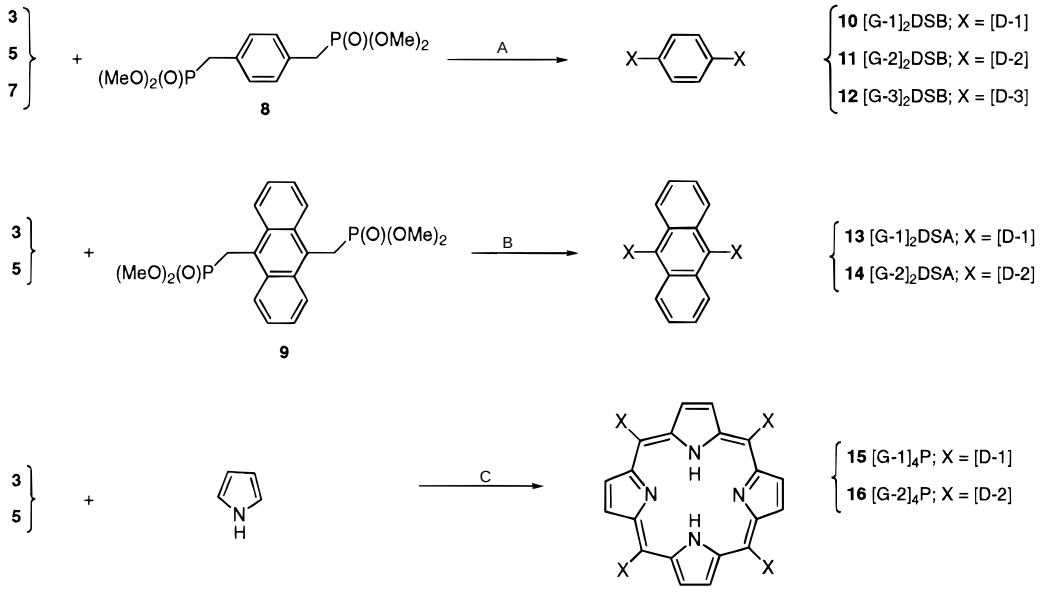
[a] Key: (A) anhydrous tetrahydrofuran, methyltriphenylphosphonium iodide, potassium *tert*-butoxide, room temperature; (B) 3,5-dibromobenzaldehyde, styrene, *trans*-di(*μ*-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II), 2,6-di-*tert*-butylcresol, anhydrous *N*,*N*-dimethylacetamide, Ar, ≈130 °C.

good charge mobility, for use as the light-emitting layer in LEDs. We chose the dendrons to contain stilbene units and distyrylbenzene, distyrylanthracene, and porphyrin cores to control the color of emission. There have been two elegant convergent syntheses of dendrons based on stilbene units.[9,10] The first relies on an iterative procedure which consists of coupling a bromobis(benzyl phosphonate) with 2 equiv of an aldehyde to give a stilbene dendron with a bromine focus, which in turn is coupled in a bis-Heck reaction with a distyrylbenzaldehyde to give a dendron with an aldehyde focus.[9] Therefore, each step "doubles" the size of the dendron giving rapid access to high generation dendrons with alternate bromo and aldehyde foci. The second route uses bis-Horner−Wadsworth−Emmons couplings and acetal deprotection as the iterative steps and gives stilbene dendrons with an aldehyde at the foci for each dendron generation.[10] In both reports, the authors have utilized 1,3,5-tris(methylenedimethylphosphonate)benzene to give one tris(distyrylbenzene)-cored dendrimer[9] and several generations of stilbene-centered dendrimers.[10] In this paper, we describe a new two-step iterative procedure for the formation of stilbene-based dendrons which is complementary to the phosphonate/Heck iterative cycle[9] and gives an aldehyde moiety at the focus of each dendron generation. In addition, we show that each dendron generation can be elaborated using the aldehyde focus to form dendrimers with different luminescent cores and we also present the preliminary studies on the photophysical properties of the luminescent dendrimers.

Results and Discussion

Dendron Formation. The iterative strategy used for the aldehyde-focused dendron synthesis is shown in Scheme 1. As illustrated, the two iterative steps for dendron formation involve a simple Wittig reaction followed by a Heck coupling to give a dendron with an aldehyde at its center. We chose the 3,5-di-*tert*-butylphenyl group to be the surface functionality as it has been shown impart solubility to large conjugated molecules including stilbene based dendrons.[9,11] The first step in the iterative procedure was the formation of 3,5-di-*tert*-butylstyrene, **2**,[12] which was prepared in an 88% yield from the reaction of 3,5-di-*tert*-butylbenzaldehyde,[13] **1**, with the methylene triphenylphosphonium ylide. The second step in the first cycle of the iterative procedure was the coupling of styrene **2** with 3,5-dibromobenzaldehyde[14] to give the first generation aldehyde-focused dendron **3**. We chose *trans*-di(*μ*-acetato)-bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium-(II) as the catalyst as it was stable to high reaction temperatures for extended periods of time.[15] After 2.5 equiv of **2** was heated with 3,5-dibromobenzaldehyde in the presence of the palladium catalyst for 26.5 h at 130 °C, dendron aldehyde **3** was isolated in a 69% yield. The

Scheme 2[a]



[a] Key: (A) potassium *tert*-butoxide, anhydrous tetrahydrofuran, room temperature, N_2 followed by iodine, toluene, Δ; (B) potassium *tert*-butoxide, anhydrous tetrahydrofuran, room temperature; (C) dry dichloromethane, trifluoroacetic acid, room temperature, followed by 2,3-dichloro-5,6-dicyano-1,4-quinone.

temperature of the reaction was critical for its success. We found that if the temperature was much lower than 130 °C, then the reaction did not take place, while if the temperature of the reaction was allowed to go significantly above 130 °C, then a greater abundance of other byproducts containing an aldehyde moiety were also observed. This reaction initially proved somewhat capricious, and in addition to the desired product, polymerization of styrene **2** was sometimes observed. The polymerization could be quite efficient, and we have isolated poly(3,5-di-*tert*-butylstyrene), with an $\bar{M}_w$ of 3.9 $\times$ 10^4 and polydispersity of 2.84, in up to a 74% yield. We found that the polymerization of styrene **2** was generally decreased when the experiments were carried out in air, suggesting that the polymerization was occurring by a radical mechanism. This was confirmed by the addition of the sterically hindered radical inhibitor 2,6-di-*tert*-butylcresol which successfully suppressed the polymerization of **3**. To form the next dendron generation the same two step procedure was used. Aldehyde **3** was reacted with the methylene triphenylphosphonium ylide to give styrene **4** in a 95% yield. Styrene **4** was then coupled with 3,5-dibromobenzaldehyde under the above Heck conditions to form the second generation dendron aldehyde **5** in a 69% yield. A similar iterative procedure was used to produce the intermediate alkene **6** and the third generation dendron aldehyde **7** in 96% and 26% yields, respectively. The latter reaction in fact went very smoothly with the low yield of the third generation dendron **7** due to the difficulty we had in isolating it in an analytically pure form.

We found that the generation number affected the way each of the aldehyde focused dendrons could be purified. Purification of the first generation aldehyde dendron **3** was relatively straightforward and achieved in two steps. First, the crude product was triturated with cold light petroleum to remove excess **2** and other byproducts. This essentially pure **3** was then recrystallized from a dichloromethane/light petroleum mixture to give pure **3**. In contrast the second generation dendron **5** required both recrystallization and chromatography for purification. Recrystallization removed all the impurities except the excess styrene **4** as adjudged by thin-layer chromatography. The difficulty arose in the separation of **4** and **5** by column chromatography on silica as they both had poor solubility in the solvent mixture required for separation. Nevertheless, they can be separated and we have prepared **5** on multigram scales. Finally, the third generation dendron **7** was purified by column chromatography over silica and could be precipitated, with difficulty, from solution when pure.

Dendrimer Formation. The aldehyde focused dendrons allow a variety of potential coupling reactions to form luminescent cored dendrimers. To form the distyrylbenzene dendrimers we coupled 2 equiv of **3**, **5**, and **7** with the bis-anion of bis(phosphonate) **8**[16] (Scheme 2). The fraction of the material containing the dendrimers was easily isolated from more polar impurities by chromatography over silica. However, the less polar fraction containing the desired *trans*,*trans*-distyrylbenzene dendrimers normally included highly fluorescent impurities that had similar polarities to each of the desired dendrimers. In the case of the first and second generation distyrylbenzene cored dendrimers **10** and **11**, we could isolate some of the trans,trans-products pure but only with difficulty and in the case of **11** in low yields. Since the impurities had similiar polarities and were highly fluorescent, we thought that the impurities could be geometrical isomers, cis,trans- and potentially cis,cis-, of the desired *trans*,*trans*-distyrylbenzene-centered dendrimers. This was confirmed by treating the impure dendrimer fractions with iodine in toluene heated at reflux. After isomerization, we were able to isolate the pure *trans*,*trans*-distyrylbenzene dendrimers **10**, **11**, and **12** in yields of 57, 59, and 55% respectively. All three dendrimers had good solubility and could be processed from solution to form good quality thin films. This is in contrast to the reported tris(distyrylbenzene)-cored dendrimer, which is equivalent in dendron generation to **12**, which showed poor solubility and could only be formed in low yield.[9]

The two distyrylanthracene-cored dendrimers **13** and **14** were formed under similar conditions to the distyryl-

benzene dendrimers. Reaction of 2 equiv of **3** or **5** with the bis-anion of anthracene bisphosphonate **9** gave **13** and **14** in isolated yields of 54% and 64% respectively. It is interesting to note that in this case we did not have the difficulty of separating cis and trans isomers. As in the case of the distyrylbenzene-centered dendrimers both **13** and **14** had good solubility and could be spin-coated from solution to form good quality films.

Formation of the porphyrin-centered polymers went surprisingly well considering the size of the aldehydes we were using. We tried both the Lindsey[17] and Rothenmund porphyrin synthesis methods and found that the former was preferable. Aldehydes **3** and **5** were condensed with pyrrole in dichloromethane in the presence of trifluoroacetic acid. The intermediate chlorins were then oxidized to the corresponding porphyrins with 2,3-dichloro-5,6-dicyano-1,4-quinone. The condensation reactions were relatively sluggish, but after several days, the porphyrin dendrimers **15** and **16** were formed in the excellent yields of 33% and 24% respectively. We found that the porphyrin-centered dendrimers also had good solubility and could be processed into good quality thin films.

As all the dendrimers have a high degree of symmetry, the assignment of their structures by ^{1}H NMR spectroscopy was generally straightforward. However, for the distyrylbenzene series analysis of the ^{1}H NMR spectra of **11** and **12** (second and third generations) was complicated by overlap of the core vinyl signals with those of the dendrons. In **11** it was possible to detect and assign the core vinyl protons among the dendron signals using a combination of one-dimensional and COSY spectra. For the third generation distyrylbenzene dendrimer **12**, the signals of the core vinyl protons were completely obscured by the dendron protons and are quoted as a range in the Experimental Section with the limits determined by the analogous protons in the first and second generation distyrylbenzene dendrimers. The structures of each of the dendrimers was confirmed by MALDI−TOF mass spectroscopy with all of the dendrimers having a molecular ion at the mass expected. In addition, gel-permeation chromatography (gpc) against polystyrene standards showed that all the dendrimers were monodisperse as would be expected from their well ordered construction. We have not yet being able to determine the exact shape of the distyrylbenzene- and distyrylanthracene-cored dendrimers, but it is conceivable that they could be essentially planar to maximize delocalization. Using simple models, it is only the third generation distyrylbenzene-cored dendrimer **12** in which steric hindrance of the surface groups can cause a twisting of the dendrimer out of plane. In contrast, the porphyrin-centered dendrimers cannot be planar due to the steric interaction of the β-pyrrolic protons with the dendrons. This means that the dendrons are held orthogonally to the plane of the porphyrin core, which in turn projects the surface groups over the plane of the porphyrin ring. This structure for the porphyrin dendrimers was confirmed by comparing the chemical shifts in the ^{1}H NMR of the *tert*-butyl groups of the dendrons, the more planar distyrylbenzene and distyrylanthracene dendrimers, and the porphyrin dendrimers **15** and **16**. The signals due to the *tert*-butyl protons in the dendrons were all in the region 1.39−1.41 ppm, and coupling the dendrons to form the distyrylanthracene and distyrylbenzene dendrimers did not move the signals of the *tert*-butyl protons out of the 1.39−1.41 ppm range. In contrast, the signals due to the *tert*-butyl groups for the first and second generation porphyrins **15** and **16** were found at 1.35 and 1.33 ppm, respectively, indicating that they are being weakly shielded and hence are over the porphyrin ring.

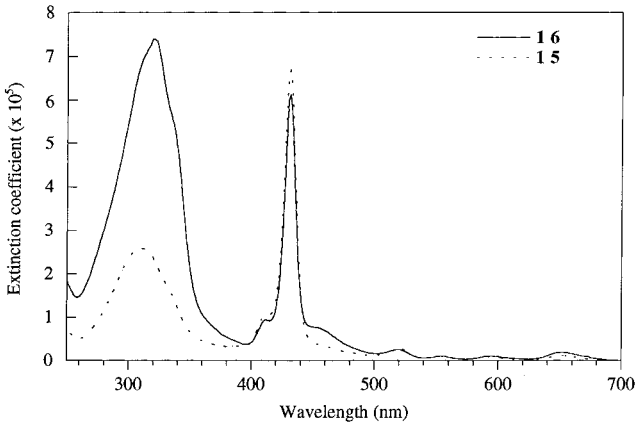


Figure 1. UV−visible spectra of the porphyrin-cored dendrimers.

Photophysical Properties. The dendrimers all had two components to their UV−visible absorption spectra. In each case there was an absorption due to the central chromophore as well as an absorption associated with the stilbene containing dendrons. We found that the ratio of the absorption of the dendron to that of the core increased as the dendrimer generation increased. This is illustrated in Figure 1 which shows the UV−visible absorption spectra of the porphyrin dendrimers **15** and **16**. The main features of the absorption of both molecules are the four Q-bands in the region 500−700 nm (which are consistent with a free-base porphyrin), the Soret band at 431 nm, and the absorption of the dendrons (310−320 nm). The absorption of the dendrons (peaks at 311 and 320 nm for **15** and **16**, respectively) is due to the constituent stilbene units. The dramatic increase in the ratio of the strength of the dendron absorption to the Soret absorption on going from the first to second generation is due to the increase in the number of stilbene units from eight per porphyrin to 24. We observed in the UV−visible absorption spectra of the aldehyde-cored dendrons only a slight red shift in the absorption maxima in going from the first to the third generation, which is consistent with the observations already reported for such systems.[9] However, there is an interesting question regarding the effect of dendrons on the electronic properties of the central chromophore. We therefore compared the absorption spectra of the unsubstituted cores with the corresponding dendrimers. With the distyrylbenzene dendrimers, there was found to be a slight red shift of the onset of absorption in going from distyrylbenzene to the first generation dendrimer.[7] However, in going from the first to the second and third generation distyrylbenzene dendrimers, there was no significant shift of the onset of absorption. In the present work, a similar effect was observed for the porphyrin dendrimers where there was a slight red shift (9 nm) in the Soret absorption in going from 5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)porphyrin (TDiBPP) to the first generation porphyrin dendrimer inspite of the dendrons being orthogonal to the plane of the porphyrin core. There was also no real change in the absorption spectrum in going from the first to the second generation porphyrin apart from a

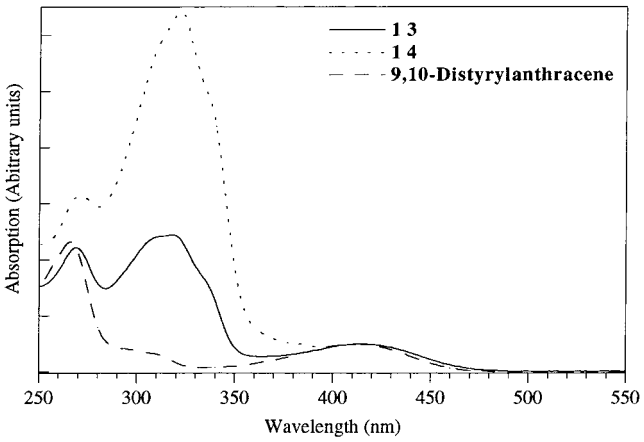


Figure 2. UV−visible spectra of 9,10-distyrylanthracenes **13** and **14**. The spectra have been normalized at the distyrylanthracene long wavelength absorption for ease of comparison.

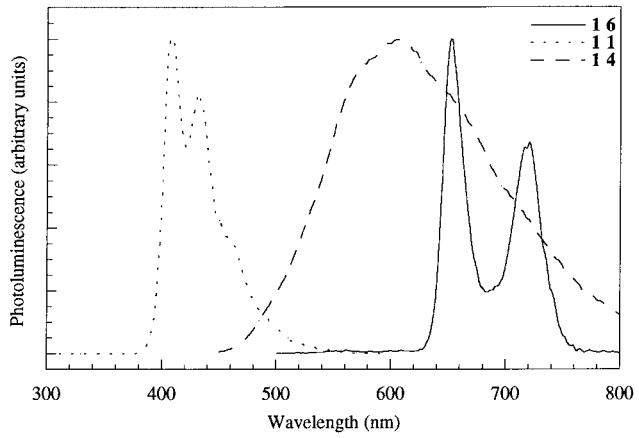


Figure 3. PL spectra of the second generation distyrylbenzene-, distyrylanthracene-, and porphyrin-cored dendrimers excited at 325, 420, and 420 nm, respectively. The spectra have been normalized for ease of comparison.

tail on the long wavelength side of the Soret band. In contrast, the dendrons had no effect on the onset of absorption or absorption maxima of the distyrylanthracene-cored (Figure 2) dendrimers. Taking into account that the distyrylanthracene-cored dendrimers can adopt a relatively planar arrangement with the dendrons, it is perhaps surprising that we do not observe a red shift similar to that seen in the distyrylbenzene and porphyrin families of dendrimer in going from the unsubstituted core to the first generation dendron. The fact that the dendrons have little effect on the absorption spectra of the core of the dendrimers is consistent with the cross-conjugation present in the dendrimers.

The solution photoluminescence (PL) spectra of the dendrimers were recorded in chloroform and the spectra of **11**, **14**, and **16** are shown in Figure 3. The PL spectra of the distyrylbenzene dendrimers all show vibronic structure[7] while the distyrylanthracene dendrimers have a broad emission spectrum. The porphyrin dendrimers have two singlet emission peaks (655 and 720 nm) which are at similar wavelengths to those observed for *meso*-tetraphenylporphyrin and correspond to the Q(0,0) and Q(0,1) transitions.[18] From these emission spectra the Commission Internationale d'Eclairage 1931 (C.I.E.) coordinates (*x*, *y*) for the second generation dendrimers (**11**, **14**, and **16**) were determined to be (0.15, 0.05), (0.51, 0.47), and (0.69, 0.31) which correspond to blue, yellow-green, and red emissions, respectively.

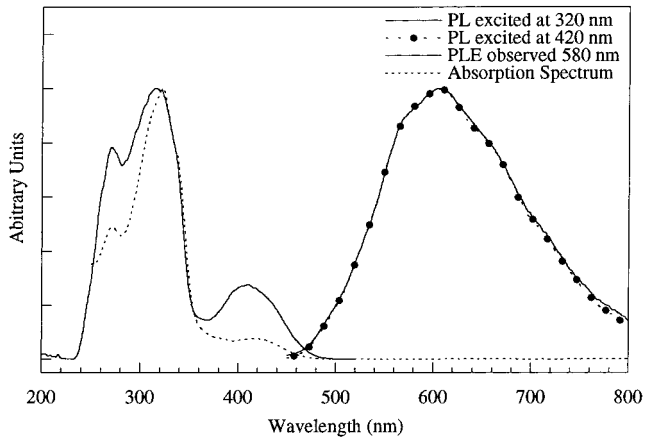


Figure 4. PL, PLE, and absorption spectra of the second generation distyrylanthracene dendrimer **14**. The spectra have been normalized for ease of comparison.

As the dendrimers have cross-conjugation, we were interested in determining whether energy transfer could occur easily from the dendrons to the core. There have been a number of reported studies on energy transfer from dendrons to a luminescent core where the dendrons contain either saturated and unsaturated components[8] or just unsaturated moieties.[19] In each case, excitation of the dendrons resulted in energy transfer from the dendron to the core. Given that the distyrylbenzene and distyrylanthracene dendrimers are relatively planar, we expected that energy could be transferred easily from the dendrons to the core inspite of the cross-conjugation. In contrast, the porphyrin dendrimers have the dendrons held orthogonally to the plane of the porphyrin, and this conformation might be expected to give rise to poor energy transfer from the dendrons to the core.

We have reported that the distyrylbenzene dendrimers emit from the distyrylbenzene core whether they were excited at the absorption wavelengths of either the dendron or the core.[7] Similar results were observed for the distyrylanthracene-cored dendrimers (Figure 4 shows the data for the second generation dendrimer). Excitation at 320 nm, where the distyrylanthracene core has weak absorbance and the stilbene dendrons strong absorbance, gave rise to a PL emission which was identical to that observed when the dendrimer was excited at 420 nm, where the distyrylanthracence core absorbs. This clearly indicates that the energy is transferred from the dendrons to the core in **14**.

To get an idea of the efficiency of energy transfer we carried out a photoluminescence excitation (PLE) experiment in which the intensity of PL from the core at 580 nm was measured as the excitation wavelength was scanned across the absorption spectrum (Figure 4). We found that since the ratio of PLE at 420 nm to that at 320 nm was greater than that of the absorbance at those wavelengths, the energy transfer from the dendrons was less than quantitative. We can use these data to make an estimate of the efficiency of energy transfer of 65 ± 10%. The same results were observed for the first generation distyrylanthracene dendrimer **13**.

The porphyrin dendrimers were excited at 300 and 420 nm, which corresponds to the stilbene dendrons and the porphyrin Soret band, respectively. We observed in both cases PL from the porphyrin core, indicating that

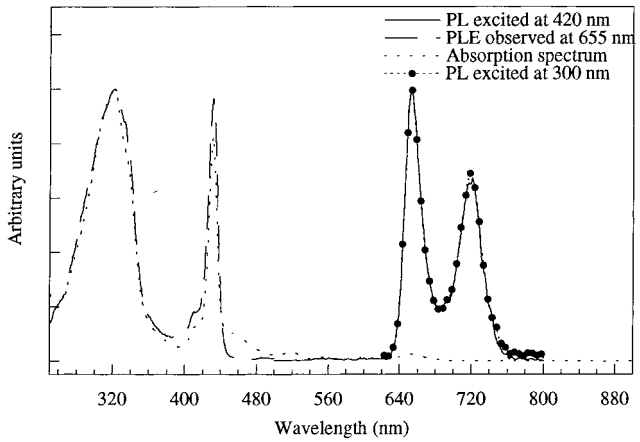


Figure 5. PL, PLE, and absorption spectra of the second generation porphyrin dendrimer **16**. The spectra have been normalized for ease of comparison.

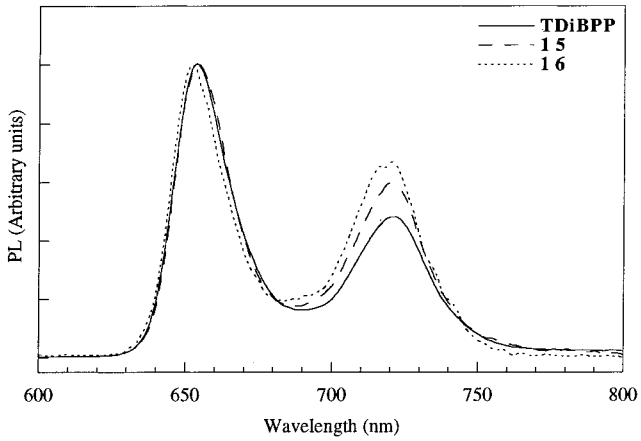


Figure 6. PL spectra of TDiBPP **15**, and **16** excited at 420 nm. The spectra have been normalized for ease of comparison.

even though the dendrons are rigid and held orthogonally to the plane of the porphyrin, energy transfer is occurring (Figure 5). In fact the similarities between the PLE and absorption spectra suggest that the energy transfer occurs with close to 100% efficiency. There were no changes in the emission wavelengths for the porphyrin PL in going from the "zeroeth" generation porphyrin dendrimer, TDiBPP, to the first and second generation porphyrin dendrimers. However, we did observe a change in the ratio of the Q(0,0) to Q(0,1) emission intensities with Q(0,1) increasing with increasing generation number (Figure 6).

Conclusion

We have successfully developed a new family of dendrimers which have luminescent cores and stilbene-containing dendrons. By selection of the core we have made dendrimers which give blue, yellow-green, and red light emissions. Importantly for our interest in using these materials in LEDs, the dendrons are capable of charge transport and all the dendrimers, independent of generation or core, could be spin-coated from solution to form optical quality thin films. This clearly shows that we have managed to disengage the processing from the electronic properties in this series of materials. We have observed that excitation of the dendrons leads to energy transfer from the dendrons to the luminescent cores. We have used a new two-step iterative procedure which gives aldehyde-centered dendrons at each cycle with the two orthogonal reactions not requiring a protecting group strategy.

Experimental Section

Measurements. NMR spectra were recorded on a Bruker DPX 400 MHz, an AM 500 MHz, or an AMX 500 MHz spectrometer: sp = surface phenyl; cp = core phenyl; cv = core vinyl; bp = branch phenyl. All *J* values are in hertz. IR spectra were recorded on a Perkin-Elmer Spectrum 1000 infrared spectrometer, and all spectra were recorded as a solution in spectroscopic grade chloroform. UV−visible spectra were recorded on Perkin-Elmer UV−visible Lambda 14P or Lambda 19 spectrometers, and all spectra were recorded as a solution in spectroscopic grade chloroform unless otherwise stated. Mass spectra were recorded on a Hewlett-Packard 1050 atmospheric pressure chemical ionization mass spectrometer (APCI) (+ve mode), a PerSeptive Biosystems Voyager Elite matrix-assisted laser desorption/ionization−time-of-flight (MALDI−TOF) from 2,5-dihydroxybenzoic acid (reflectron mode) or a Micromass TofSpec 2E MALDI−TOF from 2,5-dihydroxybenzoic acid (reflectron mode). Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected or on a Perkin-Elmer DSC-7. Microanalyses were carried out either in the Inorganic Chemistry Laboratory or the Dyson Perrins Laboratory, Oxford, U.K. Gel permeation chromatography was carried out using PLgel 20 μm Mixed-A columns (600 mm + 300 mm lengths, 7.5 mm diameter) from Polymer Laboratories calibrated with polystyrene narrow standards ($\bar{M}p$ = 1300 to 15.4 × 10^6) in tetrahydrofuran with toluene as flow marker. The tetrahydrofuran solvent was degassed with helium and pumped with a rate of 1 mL/min at 23.5 ± 2 °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. Photoluminescence spectra and photoluminescence excitation spectra of the dendrimers in chloroform solution were measured using a Perkin-Elmer LS50 fluorimeter. The peak absorbance in a 1 cm cuvette of solutions used for these measurements was close to 0.1.

[D-0]$_2$PhCHO, 3. A mixture of 3,5-dibromobenzaldehyde[14] (31.7 g, 120 mmol), **2**[12] (65.0 g, 301 mmol), anhydrous sodium carbonate (31.9 g, 301 mmol), *trans*-di(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II)[15] (244 mg, 0.26 mmol, 0.1 mol %), 2,6-di-*tert*-butylcresol (13.3 g, 60 mmol), and anhydrous *N*,*N*-dimethylacetamide (130 mL) was deoxygenated thoroughly by stirring under oil-pump vacuum followed by purging with argon several times. The reaction mixture was then heated under argon at 130 °C for 26.5 h. After cooling, ether (250 mL) and hydrochloric acid (1.5 M, 150 mL) were added carefully. The organic layer, which contained a suspension, was washed with distilled water (5 × 125 mL) and the solvent completely removed. The aqueous layers were combined and then extracted with ether (100 mL). The organic layer was separated and washed with distilled water (4 × 30 mL), and then the solvent was completely removed. The combined organic residues were triturated thoroughly with cold light petroleum (bp 40−60 °C), and the mixture was filtered. The residue was recrystallized from a dichloromethane/light petroleum mixture to give colorless crystals of **3** (44.61 g, 69%), mp 217−219 °C. Anal. Calcd for $C_{39}H_{50}O$: C, 87.6; H, 9.4. Found: C, 87.7; H, 9.7. ν_{max} ($CHCl_3$)/cm^{-1}: 1698 s (C=O), 1596 s (C=C), and 964 s (C=C−H trans). λ_{max} ($CHCl_3$)/nm: 316 (log ϵ/dm^3 mol^{-1} cm^{-1} 4.65). δ_H (500 MHz; $CDCl_3$): 1.41 (36 H, s, *t*-Bu), 7.20 and 7.34 (4 H, d, *J* = 16, vinyl H), 7.43 (2H, dd, *J* = 1.5, sp H), 7.44 (4 H, d, *J* = 1.5, sp H), 7.94 (1 H, m, cp H), 7.95 (2 H, d, *J* = 1.5, cp H), and 10.11 (1 H, s, CHO). *m*/*z* ($APCI^+$): 535 (M^+, 100%).

[D-0]$_2$PhCHCH$_2$, 4. Dry tetrahydrofuran (375 mL) was added to a mixture of methyltriphenylphosphonium iodide (50.6 g, 125 mmol) and potassium *tert*-butoxide (14.0 g, 125 mmol), and then the reaction mixture was stirred at room temperature for 15 min. [D-0]$_2$PhCHO, **3** (44.6 g, 83.4 mmol), was added, and the reaction mixture was stirred at room temperature for 90 min. The solvent was removed, and the

remaining sludge was triturated with a dichloromethane/light petroleum (bp 40−60 °C) mixture (1:9) with dendron **4** going into solution. The mixture was filtered through a plug of silica using a dichloromethane/light petroleum (bp 40−60 °C) mixture (1:9) as eluent. The filtrate was collected and the solvent completely removed. The crude product was recrystallized from a dichloromethane/methanol mixture to give white crystals of **4** (42.1 g, 95%), mp 143−145 °C. Anal. Calcd for $C_{40}H_{52}$: C, 90.2; H, 9.8. Found: C, 90.0; H, 10.0. ν_{max} ($CHCl_3$)/cm^{-1}: 1594 (C═C) and 964 (C═C−H trans). λ_{max} ($CHCl_3$)/nm: 307 sh (log ϵ/dm^3 mol^{-1} cm^{-1} 4.83), 318 (4.84), and 332 sh (4.67); δ_H (500 MHz; $CDCl_3$): 1.39 (36 H, s, *t*-Bu), 5.34 (1 H, d, $J = 11$, cv H), 5.88 (1 H, d, $J = 18$, cv H), 6.79 (1 H, dd, $J = 11$ and 18, cv H), 7.15 and 7.25 (4 H, d, $J = 16$, G-1 vinyl H), 7.38 (2 H, dd, $J = 2$, sp H), 7.42 (4 H, d, $J = 2$, sp H), 7.49 (2 H, d, $J = 1.5$, cp H), and 7.63 (1H, m, cp H). *m*/*z* ($APCI^+$): 533 (M^+, 100%).

[D-1]$_2$PhCHO, 5. A mixture of 3,5-dibromobenzaldehyde (8.21 g, 31.1 mmol), **4** (41.4 g, 77.7 mmol), anhydrous sodium carbonate (6.59 g, 62.2 mmol), *trans*-di(*μ*-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (58.3 mg, 0.062 mmol, 0.1 mol %), 2,6-di-*tert*-butylcresol (1.71 g, 7.77 mmol), and anhydrous *N*,*N*-dimethylacetamide (100 mL) was deoxygenated thoroughly by stirring under oil-pump vacuum followed by purging with argon several times. The reaction mixture was then heated under argon at 130 °C for 17 h. The reaction mixture was allowed to cool, and anhydrous *N*,*N*-dimethylacetamide (100 mL) was added. The reaction mixture was deoxygenated and then heated at 130 °C for a further 5.5 h. Anhydrous *N*,*N*-dimethylacetamide (100 mL) was then added to the reaction mixture, which was then heated at 130 °C for 1 h. Water (250 mL) was added to the reaction mixture, and the mixture was filtered. The residue was washed with water (2 × 250 mL) and then dissolved in dichloromethane (1500 mL). The organic layer was washed with distilled water (500 mL), dried over anhydrous sodium sulfate, and filtered, and the solvent was completely removed to give a cream colored solid. The crude product was recrystallized from a dichloromethane/light petroleum mixture three times. The residue was collected and purified by column chromatography over silica using chloroform/light petroleum (2:3) as eluent. The main fraction was collected, the solvent completely removed, and the residue recrystallized from a dichloromethane/light petroleum mixture to give a white solid of **5** (25.2 g, 69%). δ_H (500 MHz; $CDCl_3$): 1.41 (72 H, s, *t*-Bu), 7.20 and 7.32 (8 H, d, $J = 16$, G-2 vinyl H), 7.34 and 7.38 (4 H, d, $J = 16$, G-1 vinyl H), 7.42 (4 H, dd, $J = 1.5$, sp H), 7.46 (8 H, d, $J = 1.5$, sp H), 7.67 (4 H, s, G-1 bp H), 7.69 (2 H, s, G-1 bp H), 8.00 (3 H, s, cp H), and 10.14 (1 H, s, CHO). *m*/*z* (MALDI): 1167.7 (M^+) Data for **5** are identical to reported data.[9]

[D-1]$_2$PhCHCH$_2$, 6. Dry tetrahydrofuran (250 mL) was added to a mixture of methyltriphenylphosphonium iodide (9.87 g, 24.4 mmol) and potassium *tert*-butoxide (2.74 g, 24.4 mmol), and then the reaction mixture was stirred at room temperature for 25 min. [D-1]$_2$PhCHO, **5** (19.0 g, 16.3 mmol), and dry tetrahydrofuran (60 mL) were added, and the reaction mixture was stirred at room temperature for 2.3 h. Acetone (50 mL) was added, and then the solvent was completely removed. The crude product was triturated with a dichloromethane/light petroleum (bp 40−60 °C) mixture (1:4) with dendron **6** going into solution. The mixture was filtered through a plug of silica using a dichloromethane/light petroleum (bp 40−60 °C) mixture (1:4) as eluent. The filtrate was collected and the solvent completely removed. The residue was purified by column chromatography over silica using a dichloromethane/light petroleum mixture (3:17) as eluent. The main fraction was collected and the solvent completely removed. The residue was recrystallized from a dichloromethane/methanol mixture to give **6** (18.18 g, 96%), mp 272−275 °C. Anal. Calcd for $C_{88}H_{108}$: C, 90.7; H, 9.3. Found: C, 90.2; H, 9.3. ν_{max} ($CHCl_3$)/cm^{-1}: 1594 (C═C) and 965 (C═C−H trans). λ_{max} ($CHCl_3$)/nm: 313 sh (log ϵ/dm^3 mol^{-1} cm^{-1} 5.19), 322 (5.23), and 336 sh (5.12). δ_H (400 MHz; $CDCl_3$): 1.41 (72 H, s, *t*-Bu), 5.38 (1 H, d, $J = 11$, cv H), 5.91 (1 H, d, $J = 18$, cv H), 6.82 (1 H, dd, $J = 11$ and 18, cv H), 7.19 and 7.31 (8 H, d, $J = 16$, G-2 vinyl H), 7.29 (4 H, s, G-1 vinyl H), 7.40 (4 H, dd, $J = 1.5$, sp H), 7.45 (8 H, d, $J = 1.5$, sp H), 7.55 (2 H, s, cp H), 7.66 (6 H, s, G-1 bp H), and 7.70 (1 H, s, cp H). *m*/*z* (MALDI): 1166 (M^+, 100%).

[D-2]$_2$PhCHO, 7. A mixture of [D-1]$_2$PhCHCH$_2$, **6** (4.87 g, 4.18 mmol), 3,5-dibromobenzaldehyde (441 mg, 1.67 mmol), anhydrous sodium carbonate (354 mg, 3.34 mmol), 2,6-di-*tert*-butylcresol (122 mg, 0.554 mmol), *trans*-di(*μ*-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (3.1 mg, 0.003 mmol), and anhydrous *N*,*N*-dimethylacetamide (30 mL) was deoxygenated thoroughly by stirring under oil-pump vacuum followed by purging with argon several times. The reaction mixture was then heated in an oil bath at 130 °C under argon for 39 h. After cooling, dichloromethane (200 mL), distilled water (200 mL), and hydrochloric acid (3 M, 50 mL) were added. The aqueous layer was separated and extracted with dichloromethane (3 × 30 mL). The organic fractions were combined, washed with water (3 × 250 mL), dried over anhydrous sodium sulfate, and filtered, and the solvent was completely removed. The residue was purified by column chromatography over silica using a dichloromethane/light petroleum mixture (1:4) as eluent. The main fraction was collected and the solvent completely removed. The residue was precipitated from a dichloromethane/methanol mixture, with precipitation initiated by cooling the solution to approximately −20 °C before being driven to completion by the addition of excess methanol, to give a white solid of **7** (1.04 g, 26%), mp 248−253 °C. Anal. Calcd for $C_{183}H_{218}O$: C, 90.3; H, 9.0. Found: C, 89.65; H, 8.8. ν_{max} ($CHCl_3$)/cm^{-1}: 1700 (C═O), 1594 (C═C), and 965 (C═C−H trans). λ_{max} ($CHCl_3$)/nm: 323 (log ϵ/dm^3 mol^{-1} cm^{-1} 5.56) and 340 sh (5.46). δ_H (500 MHz; $CDCl_3$): 1.39 (144 H, s, *t*-Bu), 7.20 and 7.31 (16 H, d, $J = 16$, G-3 vinyl H), 7.31−7.40 (20 H, s, G-1 and G-2 vinyl H and sp H), 7.44 (16 H, d, $J = 1.4$, sp H), 7.67 (12 H, s, G-2 bp H), 7.70 (4 H, s, G-1 bp H), 7.76 (2 H, s, G-1 bp H), 7.99 (1 H, s, cp H), 8.04 (2 H, d, $J = 1$, cp H), and 10.17 (1 H, s, CHO). *m*/*z* (MALDI): 2433 ((M^+Na)$^+$, 100%).

9,10-Bis(methylenedimethylphosphonate)anthracene, 9. A mixture of 9,10-bis(chloromethyl)anthracene[20] (5.00 g, 18.2 mmol) and trimethyl phosphite (18 mL, 152.6 mmol) was heated at reflux for 16 h. The reaction mixture was allowed to cool, and the reaction mixture was filtered. The yellow residue was washed thoroughly with light petroleum (bp 40−60 °C). The crude product was recrystallized from a dichloromethane/light petroleum mixture to give **9** (6.22 g, 81%), mp 174−178 °C. Anal. Calcd for $C_{20}H_{24}O_6P_2$: C, 56.9; H, 5.7. Found: C, 56.9; H, 5.7. ν_{max} ($CHCl_3$)/cm^{-1}: 1253 (P═O), 1061 (P−O−C), 1039 (P−O−C), 1024 (P−O−C), and 904 (P−O). λ_{max} ($CHCl_3$)/nm: 264 (log ϵ/dm^3 mol^{-1} cm^{-1} 5.16), 361 (3.88), 391 (4.13), and 402 (4.13). δ_H (500 MHz; $CDCl_3$): 3.51 (12 H, d, $J = 11$, OMe), 4.23 (4 H, d, $J = 20$, CH_2), 7.59 (4 H, m, anthracenyl H), and 8.35 (4 H, m, anthracenyl H). *m*/*z* ($APCI^+$): 423 (MH^+, 100%).

[G-1]$_2$DSB, 10. Dry tetrahydrofuran (3 mL) was added to a mixture of [D-0]$_2$PhCHO, **3** (100 mg, 0.187 mmol), 1,4-bis(methylenedimethylphosphonate)benzene, **8**,[16] (28.7 mg, 0.089 mmol), and potassium *tert*-butoxide (25 mg, 0.22 mmol) under nitrogen. The reaction mixture was then stirred at room temperature in the dark for 16 h. The solvent was completely removed, and ether (30 mL) and distilled water (30 mL) were added to the residue. The organic layer was separated and washed with water (3 × 30 mL), dried over anhydrous sodium sulfate, and filtered, and the solvent was completely removed. The crude product was isomerized with catalytic iodine in toluene (10 mL) heated at reflux for 17 h. The solvent was completely removed, and the crude product was purified by column chromatography over silica using a dichloromethane/light petroleum/triethylamine mixture (20:180:1) as eluent. The main fraction was collected and the solvent completely removed. The residue was recrystallized from a dichloromethane/methanol mixture to give **10** (58 mg, 57%), mp 280 °C. Anal. Calcd for $C_{86}H_{106}$: C, 90.6; H, 9.4. Found: C, 89.9; H, 9.3. ν_{max} ($CHCl_3$)/cm^{-1}: 1593 (C═C) and 964 (C═C−H trans). λ_{max} ($CHCl_3$)/nm: 325 (log ϵ/dm^3 mol^{-1} cm^{-1} 5.07), 336 sh (5.03), 367 (4.88), and 390 sh (4.67); δ_H (500 MHz; $CDCl_3$): 1.40 (72 H, s, *t*-Bu), 7.18 and 7.29 (8 H, d, $J = 16$, G-1 vinyl

H), 7.22 and 7.27 (4 H, d, $J = 16$, core vinyl H), 7.40 (4 H, dd, $J = 1.5$, sp H), 7.44 (8 H, d, $J = 1.5$, sp H), 7.60 (4 H, s, cp H), 7.62 (4 H, s, branch cp H), and 7.64 (2 H, s, branch cp H). *m/z* (MALDI): 1139 (M^+, 100%).

[G-2]$_2$DSB, 11. Dry tetrahydrofuran (3 mL) was added to a mixture of of [D-1]$_2$PhCHO, **5** (100 mg, 0.086 mmol), **8** (13.1 mg, 0.041 mmol), and potassium *tert*-butoxide (11.4 mg, 0.102 mmol) under nitrogen. The reaction mixture was stirred at room temperature in the dark for 15 h. The solvent was completely removed, and ether (30 mL), dichloromethane (20 mL) and distilled water (30 mL) were added to the residue. The organic layer was separated and washed with water (2 × 30 mL), dried over anhydrous sodium sulfate, and filtered, and the solvent was completely removed. The crude product was isomerized with catalytic iodine in toluene (10 mL) heated at reflux for 17 h. The solvent was completely removed, and the crude product was purified by column chromatography over silica using a dichloromethane/light petroleum/triethylamine mixture (20:80:1) as eluent. The main fraction was collected and the solvent completely removed to give **11** (58 mg, 59%). A sample for analysis was recrystallized from a dichloromethane/light petroleum mixture, mp 314 °C. Anal. Calcd for $C_{182}H_{218}$: C, 90.9; H, 9.1. Found: C, 90.2; H, 9.2. ν_{max} ($CHCl_3$)/cm^{-1}: 1593 (C═C) and 965 (C═C−H trans). λ_{max} ($CHCl_3$)/nm: 323 (log ϵ/dm^3 mol^{-1} cm^{-1} 5.49), 336 sh (5.43), 370 sh (4.97), and 392 sh (4.70). δ_H (500 MHz; CD_2Cl_2): 1.40 (144 H, s, *t*-Bu), 7.24 and 7.34 (16 H, d, $J = 16$, G-2 vinyl H), 7.31 and 7.36 (4 H, d, $J = 16$, core vinyl H), 7.38 (8 H, s, G-1 vinyl H), 7.41 (8 H, dd, $J = 1.5$, sp H), 7.47 (16 H, d, $J = 1.5$, sp H), 7.68 (4 H, s, cp H), 7.70 (12 H, s, G-1 bp H), and 7.73−7.75 (6 H, branch cp H). *m/z* (MALDI): 2406 (M^+, 100%).

[G-3]$_2$DSB, 12. Dry tetrahydrofuran (7 mL) was added to a mixture of of [D-2]$_2$PhCHO, **7** (239 mg, 0.099 mmol), **8** (15.2 mg, 0.047 mmol), and potassium *tert*-butoxide (22.3 mg, 0.198 mmol) under nitrogen. The reaction mixture was stirred at room temperature in the dark for 16 h. The solvent was completely removed, and ether (20 mL) and distilled water (15 mL) were added to the residue. The organic layer was separated and washed with distilled water (2 × 15 mL), dried over anhydrous sodium sulfate,and filtered, and the solvent was completely removed. The crude product was purified by column chromatography over silica using a dichloromethane/light petroleum/triethylamine mixture (30:70:1) as eluent. The main fraction was collected and the solvent completely removed to give impure [G-3]$_2$DSB. The impure [G-3]$_2$DSB was isomerized with catalytic iodine in toluene (20 mL) heated at reflux for 16 h. The solvent was completely removed, and the crude product was purified by column chromatography over silica using a dichloromethane/light petroleum/triethylamine mixture (20:80:1) as eluent. The main fraction was collected and the solvent completely removed to give **12** (129 mg, 55%). A sample for analysis was precipitated from dichloromethane by the addition of an excess of methanol: mp 240−250 °C. Anal. Calcd for $C_{374}H_{442}$: C, 91.0; H, 9.0. Found: C, 90.7; H, 9.4. ν_{max} ($CHCl_3$)/cm^{-1}: 1594 (C═C) and 965 (C═C−H trans). λ_{max} ($CHCl_3$)/nm: 323 (log ϵ/dm^3 mol^{-1} cm^{-1} 5.88), 334 sh (5.81), 365 sh (5.14), and 387 sh (4.79). δ_H (500 MHz; CD_2Cl_2): 1.37 (288 H, s, *t*-Bu), 7.22 and 7.33 (32 H, d, $J = 16$, G-3 vinyl H), 7.25−7.40 (4 H, core vinyl H), 7.38 (16 H, dd, sp H), 7.40 (16 H, s, G-2 vinyl H), 7.42 (8 H, s G-1 vinyl H), 7.45 (32 H, d, $J = 1.5$, sp H), 7.70 (28 H, s, cp H and G-2 bp H), and 7.77 and 7.79 (18 H, s, G-1 bp H and branch cp H). *m/z* (MALDI): 4939 (MH^+, 100%).

[G-1]$_2$DSA, 13. Dry tetrahydrofuran (2 mL) was added to a rapidly stirred mixture of **9** (39.5 mg, 0.94 mmol), potassium *tert*-butoxide (22 mg, 0.20 mmol), and [D-0]$_2$PhCHO **3** (100 mg, 0.19 mmol). The reaction mixture was stirred at room temperature for 85 min. The solvent was completely removed, and the crude product (925 mg) was purified by column chromatography over silica using a dichloromethane/light petroleum (bp 40−60 °C) mixture (3:17) as eluent. The main fraction was collected and the solvent completely removed to give a yellow solid of **13** (63 mg, 54%). A sample for analysis was recrystallized from a dichloromethane/methanol mixture: mp 284−294 °C dec. Anal. Calcd for $C_{94}H_{110}$: C, 91.1; H, 8.9. Found: C, 90.6; H, 9.2. ν_{max} ($CHCl_3$)/cm^{-1}: 1593 (C═C) and 964 (C═C−H trans). λ_{max} (CH_2Cl_2)/nm: 268 (log ϵ/dm^3 mol^{-1} cm^{-1} 4.95), 309 sh (4.96), 316 (4.96), 333 sh (4.82), and 413 (4.25). δ_H (400 MHz; $CDCl_3$): 1.40 (72 H, s, *t*-Bu), 7.05 and 8.10 (4 H, d, $J = 16$, core vinyl H), 7.25 and 7.35 (8 H, d, $J = 16$, G-1 vinyl H), 7.40 (4 H, dd, $J = 1.5$, sp H), 7.42 (8 H, d, $J = 1.5$, sp H), 7.55 (4 H, m, anthracenyl H), 7.76 (2 H, s, branch cp H), 7.78 (4 H, s, branch cp H), and 8.50 (4 H, m, anthracenyl H). *m/z* (MALDI): 1239 (M^+, 100%).

[G-2]$_2$DSA, 14. Dry tetrahydrofuran (4 mL) was added to a mixture of **9** (36.2 mg, 0.086 mmol), [D-1]$_2$PhCHO, **5** (200 mg, 0.17 mmol), and potassium *tert*-butoxide (24 mg, 0.21 mmol). The reaction mixture was stirred in the dark at room temperature under argon for 2 h. The solvent was completely removed, and the crude product was purified by column chromatography over silica using a dichloromethane/light petroleum/triethylamine mixture (20:80:1) as eluent. The main fraction was collected and the solvent completely removed. The residue was recrystallized from a dichloromethane/methanol mixture to give a yellow solid of **14** (137 mg, 64%), mp 292 °C dec. Anal. Calcd for $C_{190}H_{222}$: C, 91.1; H, 8.9. Found: C, 90.9; H, 9.25. ν_{max} ($CHCl_3$)/cm^{-1}: 1593 (C═C) and 965 (C═C−H trans). λ_{max} (CH_2Cl_2)/nm: 269 (log ϵ/dm^3 mol^{-1} cm^{-1} 5.15), 310 sh (5.43), 322 (5.47), 334 sh (5.37), and 414 (4.40). δ_H (500 MHz; $CDCl_3$): 1.40 (144 H, s, *t*-Bu), 7.08 and 8.13 (4 H, d, $J = 16$, core vinyl H), 7.20 and 7.32 (16 H, d, $J = 16$, G-2 vinyl H), 7.39 (16 H, s, sp and G-1 vinyl H), 7.45 (16 H, d, $J = 1.5$, sp H), 7.58 (4 H, m, anthracenyl H), 7.67 (4 H, s, G-1 bp H), 7.70 (8 H, s, G-1 bp H), 7.82 (2 H, s, branch cp H), 7.84 (4 H, s, branch cp H), and 8.52 (4 H, m, anthracenyl H). *m/z* (MALDI): 2505 (M^+, 100%).

[G-1]$_4$P, 15. A solution of [D-0]$_2$PhCHO, **3** (100 mg, 0.19 mmol), distilled pyrrole (13 μL, 0.19 mmol), and trifluoroacetic acid (14.5 μL, 0.19 mmol) in dry dichloromethane (14 mL) was stirred in the dark for 66 h under nitrogen. 2,3-Dichloro-5,6-dicyano-1,4-quinone (146 mg, 0.64 mmol) was added, and the reaction mixture was stirred for a further 40 min. Sodium hydrogen carbonate (1.0 g, 11.9 mmol) was added and the solvent was completely removed. The crude product was purified by column chromatography over silica using a dichloromethane/light petroleum (bp 40−60 °C) mixture (3:17) as eluent. The main fraction was collected and the solvent completely removed to give **15** (36 mg, 33%). A sample for analysis was recrystallized from a dichloromethane/methanol mixture: mp 255−260 °C dec. Anal. Calcd for $C_{172}H_{206}N_4$: C, 88.7; H, 8.9; N, 2.4. Found: C, 88.2; H, 8.9; N, 2.0. ν_{max} ($CHCl_3$)/cm^{-1}: 3322 (NH), 1593 (C═C), and 964 (C═C−H trans). λ_{max} ($CHCl_3$)/nm: 311 (log ϵ/dm^3 mol^{-1} cm^{-1} 5.40), 412 sh (4.98), 431 (5.82), 520 (4.46), 555 (3.95), 592 (3.82), and 648 (3.63). δ_H (500 MHz; $CDCl_3$): −2.61 (2H, s, NH), 1.35 (144 H, s, *t*-Bu), 7.37 (8 H, bdd, sp H), 7.41 (8 H, d $J = 16$, vinyl H), 7.44−7.47 (24 H, vinyl and sp H), 8.15 (4 H, bs, branch cp H), 8.34 (8 H, d, $J = 1$, branch cp H), and 9.06 (8 H, s, pyrrolic H). *m/z* (MALDI): 2330 (M^+, 100%).

[G-2]$_4$P, 16. Dry dichloromethane (90 mL) was distilled into a flask containing pyrrole (58 μL, 0.86 mmol) and [D-1]$_2$PhCHO, **5** (1.00 g, 0.86 mmol), under nitrogen. Trifluoroacetic acid (66 μL, 0.86 mmol) was added, and the reaction mixture was stirred in the dark for 5 days under nitrogen. 2,3-Dichloro-5,6-dicyano-1,4-quinone (146 mg, 0.64 mmol) was added, and the reaction mixture was stirred for a further 40 min. The solution was washed with saturated sodium bicarbonate solution (100 mL), and the aqueous layer was separated and extracted with dichloromethane (2 × 30 mL). The combined organic layers were washed with distilled water (4 × 50 mL), dried over anhydrous sodium sulfate, and filtered, and the solvent was completely removed. The crude product was purified by column chromatography over silica using a dichloromethane/light petroleum (bp 60−80 °C) mixture (3:17) as eluent. The main fraction was collected and the solvent completely removed. The residue was recrystallized from a dichloromethane/methanol mixture to give a brown solid of **16** (249 mg, 24%), mp (DSC) 270 °C. Anal. Calcd for $C_{364}H_{430}N_4$: C, 89.9; H, 8.9; N, 1.15. Found: C, 89.05; H, 8.7; N, 1.1. ν_{max} ($CHCl_3$)/cm^{-1}: 3321 (NH), 1593 (C═C), and 964 (C═C−H

trans). λ_{max} ($CHCl_3$)/nm: 320 (log ϵ/dm^3 mol^{-1} cm^{-1} 5.86), 411 (5.06), 431 (5.78), 519 (4.42), 555 (4.01), 592 (3.89), and 648 (3.67). δ_H (500 MHz; $CDCl_3$): −2.50 (2 H, s, NH), 1.33 (144 H, s, *t*-Bu), 7.17 and 7.28 (32 H, d, J = 16, G-2 vinyl H), 7.34 (16 H, dd, J = 1.5, sp H), 7.39 (32 H, d, J = 1.5, sp H), 7.52 and 7.60 (16 H, d, J = 16, G-1 vinyl H), 7.66 (8 H, s, G-2 bp H), 7.69 (16 H, s, G-2 bp H), 8.29 (4 H, s, G-1 bp H), 8.43 (8 H, s, G-1 bp H), and 9.17 (8 H, s, pyrrolic H). *m*/*z* (MALDI): 4861 (M^+, 100%).

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