The development of phenylethylene dendrons for blue phosphorescent emitters

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New high triplet energy dendrons based on 1,2-diphenylethylene with and without 2-ethylhexyloxy surface groups have been developed for deep blue phosphorescent iridium(III) dendrimers. The *fac*-tris[1-methyl-5-(4-fluoro)phenyl-3-*n*-propyl-1*H*-[1,2,4]triazolyl]iridium(III)-cored dendrimers, bearing first generation 1,2-diphenylethylene dendrons on the ligand triazolyl and phenyl rings, were prepared in excellent yields, employing Sonogashira cross-couplings and palladium catalysed hydrogenation as the key synthetic steps. Both dendrimers showed good thermal stability although the flexible nature of the dendrons led to the materials having low glass transition temperatures. Dendrimer **15** (without the surface groups) emitted good blue phosphorescence with a solution photoluminescence quantum yield (PLQY) of 46%, Commission Internationale de l'Eclairage (CIE) co-ordinates of (0.15, 0.14) and photoluminescence peaks at 441 and 468 nm. The solution PLQY was 50% higher than the parent iridium(III) complex showing that the high triplet energy of the diphenylethylene dendrons does not quench the luminescence of the iridium(III) complex core. Dendrimer **34**, which has the surface groups, had a film PLQY of 49% and CIE co-ordinates of (0.16, 0.19) with PL peaks at 441 and 469 nm.

Introduction

Light-emitting dendrimers have played an important role in the development of highly efficient solution processed organic light-emitting diodes (OLEDs). Dendrimers are comprised of cores, dendrons, and at the distal ends of the dendrons surface groups can often be found. The dendrons themselves are made up of branching points and often linking groups that connect the individual branching points. For example, Fréchet type dendrons have benzene branching points and methylenoxy linking groups.[1] The dendrons can play an important role in the properties of a dendrimer either through the generation that is used and/or the branching and linking units from which they are made.[2] We have primarily been interested in developing dendrimers for organic optoelectronics applications.[3,4] Within this area conjugated dendrons including stilbenyl[5] or diphenylacetylenyl[6] units with phenyl branching and vinyl and acetylenyl linkers, respectively, and biphenyl,[7,8] bithiophenyl,[9] and carbazolyl moieties[10–13] have played an important role in the development of working devices. The latter three dendron types are differentiated in that the (hetero)aryl units are contiguously attached in the dendrons. One of the key elements of these latter dendrons is that they give rigidity to the dendrimers, which enables control over the intermolecular interactions that are critical for device performance, and in some cases the dendrons themselves are also electroactive.[10,13]

Dendrimers that are composed of conjugated branching points and non-conjugated linking units have been studied less for optoelectronic applications. Benzene,[14] triazine,[15] and phosphazene[16] branching groups in conjunction with alkoxy linking units, and carbazolyl branching points with ethylene linkers[17] have been used in dendrons that have given rise to light-emitting dendrimers used in OLEDs. One of the issues of the alkoxy-linked dendrons is the long-term stability of the ether linkage. 1,2-Diphenylethylene based dendrons are isostructural with the moieties in Fréchet dendrons but have not yet been reported.

As part of our program on light-emitting dendrimer development for OLEDs, we have been interested in developing solution processible deep blue phosphorescent emitters. To this end we have developed *fac*-tris(1-methyl-5-phenyl-3-*n*-propyl-1*H*-[1,2,4]triazolyl)iridium(III) complexes that show good blue phosphorescence at room temperature.[18] However, small molecule phosphorescent emitters generally require the use of a host to control the intermolecular interactions that can lead to the quenching of the luminescence.[19] In addition, it has been recently found that bis-cyclometalated iridium(III) complexes undergo isomerisation during vacuum processing meaning that their integrity can be lost during device manufacturing.[20] By incorporating light-emitting chromophores at the core of a dendrimer, it has been found that the dendritic architecture can control the interactions that govern device efficiency, and that small molecule chromophores can be made solution processible.[21] Biphenyl-based dendrons have been successfully used for red,[22] green,[23] and sky-blue emissive dendrimers[24] but more recently it has been reported that the biphenyl dendrons quench the deep blue emission from iridium(III) complexes in the solid state.[25,26] The

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quenching has been attributed to the fact that the triplet energy of the biphenyl dendrons is near to that of the emissive cores, and hence the dendrons act as a pathway for energy loss.

In this paper we investigate 1,2-diphenylethylene based dendrons as high triplet energy dendrons that could address this problem of quenching by the dendrons, and would therefore be suitable for use with deep blue emissive iridium(III) complexes. We show that this approach enables good room temperature photoluminescence quantum yields to be achieved for blue phosphorescent materials. We find that the ethylene linkers within the dendrons and the presence of surface groups have a strong effect on the thermal properties of the dendrimers. In addition, we discuss the effect of the attached dendrons on the photophysical and electronic properties of the dendrimers and compare them with a dendrimer with the same emissive core and surface groups but biphenyl-based dendrons, and the simple parent and methyl substituted complexes.

Results and discussion

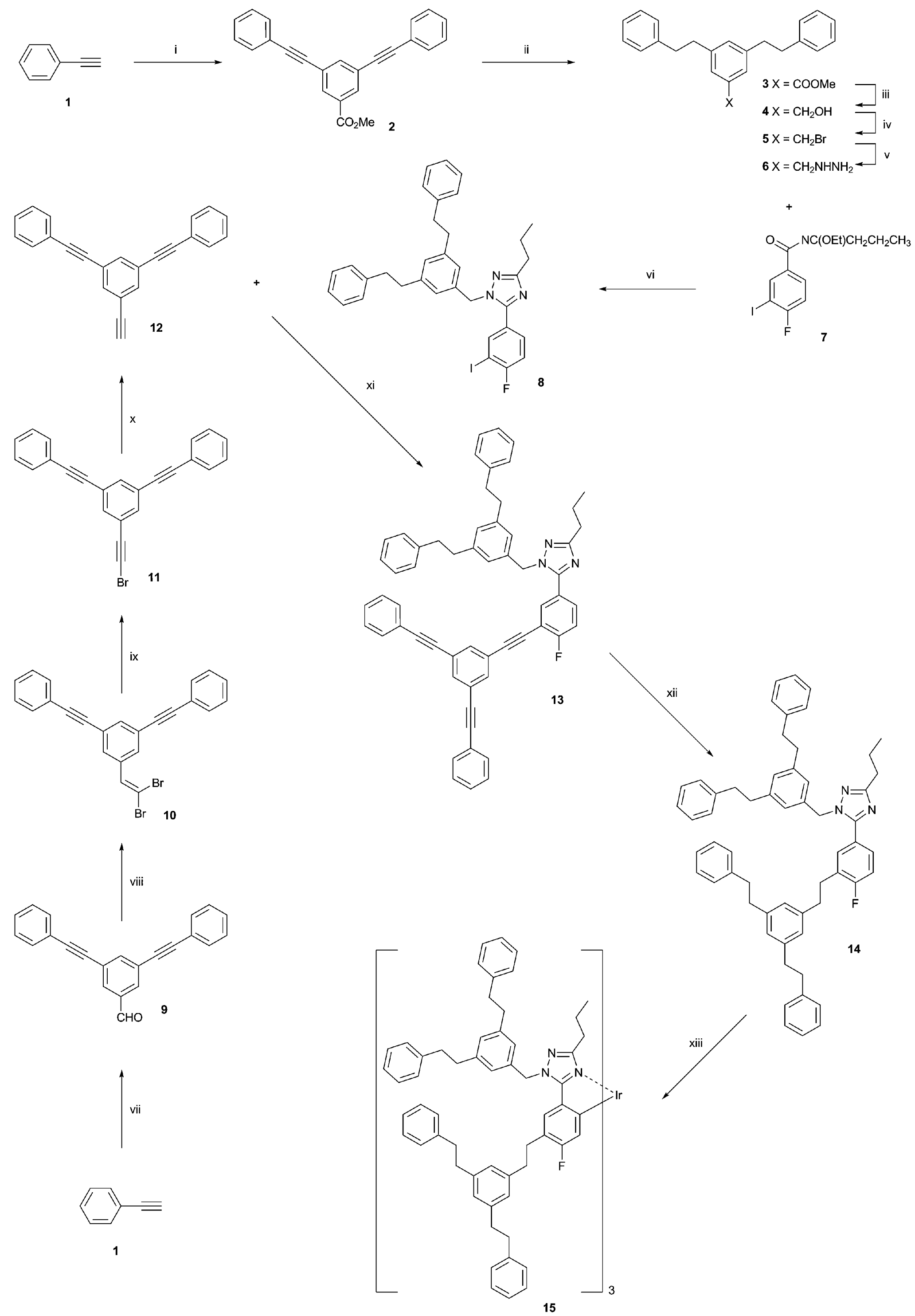
In previous work on light-emitting phosphorescent dendrimers, it has been found that the attachment of dendrons to both aromatic rings of the ligands encapsulates the light-emitting iridium(III) complex at the core more efficiently than a single dendron per ligand.[21] Therefore, the dendrimers in this study have been designed to incorporate a dendron on the triazolyl and phenyl rings of the core *fac*-tris[1-methyl-5-(4-fluoro)phenyl-3-*n*-propyl-1*H*-[1,2,4]triazolyl]iridium(III) complex **35**. This iridium(III) complex was chosen as the core because it emits deep blue phosphorescence at room temperature with CIE co-ordinates of (0.16, 0.13).[18] We chose to form the 1,2-diphenylethylene units within the dendrons by hydrogenation of diphenylacetylene[27] rather than stilbene[28,29] units as the former can be prepared under milder conditions and with excellent yields.[30,31]

Synthesis and physical properties

The light-emitting dendrimers (**15** and **34**) were prepared by first generating a doubly dendronised ligand [a dendron on each (hetero)aromatic moiety of the ligand], followed by complexation with iridium(III) (Schemes 1 and 2). The dendrimers differ in that **34** has 2-ethylhexyloxy surface groups whilst **15** does not. The 2-ethylhexyloxy surface groups increase the solubility of dendrimers with conjugated dendrons, and it is likely that they also play an important role in controlling the intermolecular interactions of the emissive cores in the solid state. Although the basic strategy for the formation of the two dendrimers is essentially the same, given the number of steps involved, they will be discussed separately for clarity.

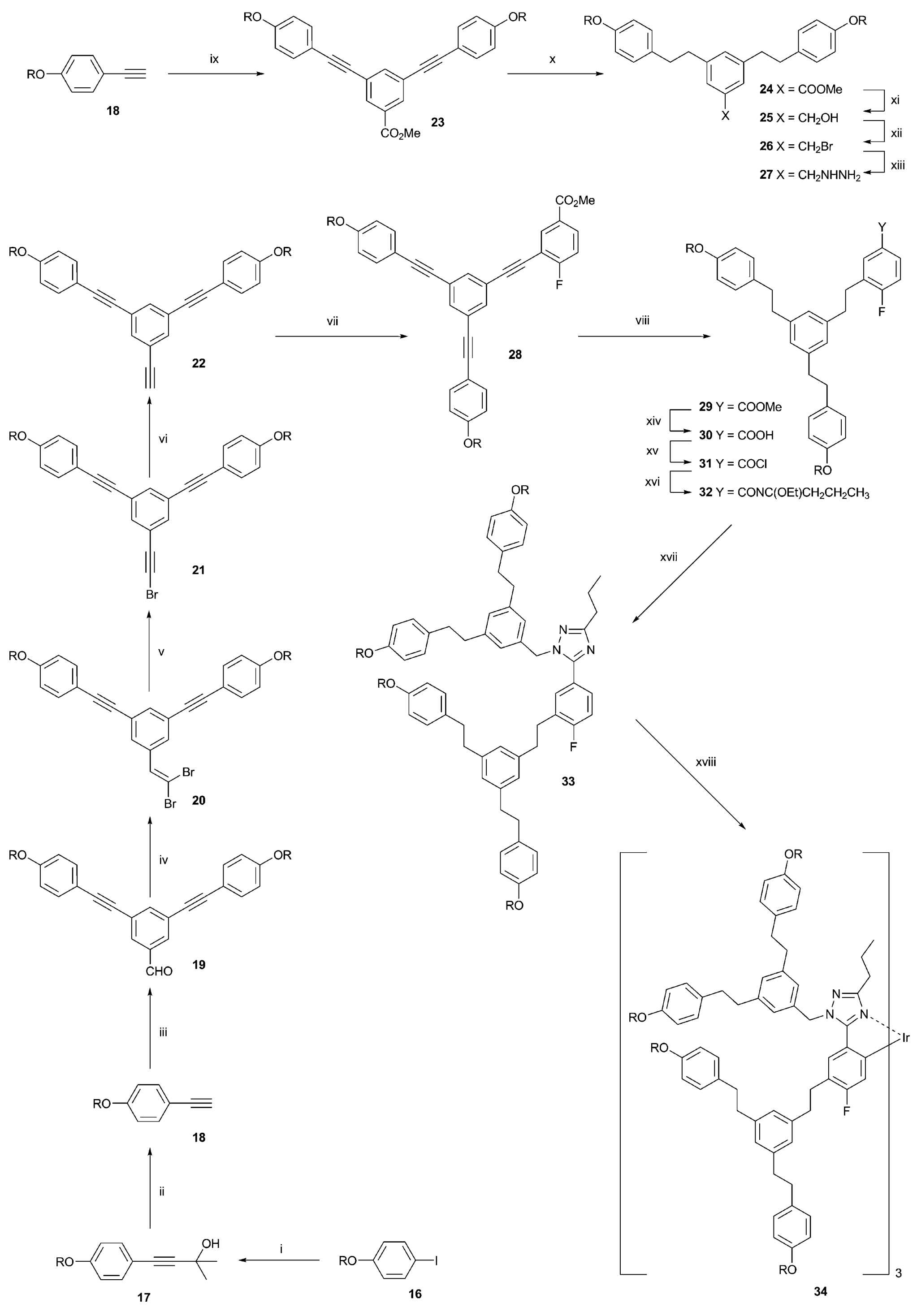
The synthesis of the doubly dendronised ligand of **15** (Scheme 1) involved attachment of a dendron to the ligand phenyl ring prior to hydrogenation with the second dendron incorporated into the ligand during the cyclisation reaction to form the triazolyl ring. The synthesis of the first generation benzylbromide focussed 1,2-diphenylethylene dendron **5**, required for the formation of the triazolyl ring of the ligand, started with commercially available methyl-3,5-diiodobenzoate. An excess of phenylacetylene **1** was reacted with methyl-3,5-diiodobenzoate under Sonogashira conditions to give **2** with an ester moiety at the focus in an excellent yield of 99%. The acetylenyl groups in **2** were then hydrogenated with a palladium on carbon catalyst to give the corresponding 1,2-diphenylethylene dendron **3** in an 87% yield. Reduction of the ester group of **3** with lithium aluminium hydride furnished the benzyl alcohol focussed dendron **4** in a 97% yield and subsequent treatment with phosphorus tribromide at approximately 90 °C gave the benzylbromide focussed dendron **5** in a 99% yield. The next part of the synthesis was the generation of the phenylacetylene dendron **12**, required for the dendronisation of the phenyl ring of the ligand. Phenylacetylene **1** was coupled with 3,5-dibromobenzaldehyde under Sonogashira reaction conditions at 76 °C for 2.5 days to give the first generation aldehyde focussed dendron **9** in an 81% yield. For the conversion of the first generation focussed aldehyde **9** into its acetylene derivative **12**, we found that carrying out the Corey–Fuchs reaction with isolation of the 1,1-dibromovinyl **10** (90%) and bromoacetylene **11** (97%) intermediates gave a very good overall yield of 80% of the acetylenyl focussed first generation dendrimer **12**.

With the two dendrons in hand, there were now two different approaches toward the formation of the doubly dendronised ligand **14**. The first method was to couple **12** with methyl-4-fluoro-3-iodobenzoate followed by hydrogenation and elaboration of the ester group to form the required *N*-benzoylbutanimidic acid ethyl ester necessary for the formation of the triazolyl ring. Although we initially followed this route we found that the cyclisation step to form the triazolyl ring was capricious and we were only able to isolate the doubly dendronised ligand **14** in low yields of between 5–15%. We therefore developed a slightly different strategy where the mono-dendronised ligand with the dendron on the triazolyl ring **8** was formed first. The benzylbromide focussed dendron **5** was converted to the corresponding hydrazine **6**, which was then reacted with the preformed *N*-4-fluoro-3-iodobenzoylbutanimidic acid ethyl ester **7** (formed from hydrolysis of the methyl ester of methyl-4-fluoro-3-iodobenzoate, conversion to the acid chloride, and subsequent reaction with ethyl butyrimidate hydrochloride) to give the mono-dendronised ligand **8** in a 64% yield with respect to **5**. In principle two isomers of the triazole ring could form and the structure of **8** was assigned by comparison with the ^{1}H NMR spectrum of the non-dendronised ligand.[18] A Sonogashira cross-coupling of **8** with **12** then gave the doubly dendronised ligand **13** in a 79% yield, and a subsequent hydrogenation over palladium on charcoal gave the desired ligand with two first generation 1,2-diphenylethylene dendrons, **14**, in an 86% yield. The final step in the synthesis of dendrimer **15**, without the surface groups, was the complexation of the doubly dendronised ligand with iridium(III). This was achieved using the standard two-step procedure.[32] In the first step **14** was reacted with iridium(III) chloride trihydrate in a water/2-(*n*-butoxy)ethanol mixture heated at reflux and then the intermediate chloro-bridged dimer was reacted with an excess of ligand of **14** in the presence of silver trifluoromethanesulfonate in the melt. Under these conditions, the iridium(III) dendrimer **15** was formed in a good yield of 69% for the two steps. **15** was determined as the *facial* isomer by the symmetry associated with the ^{1}H NMR spectrum. The symmetry in the spectrum of **15** was the same as that for complex **35** (Fig. 1), which has been unambiguously assigned as the *facial* isomer from an X-ray crystal structure.[18]



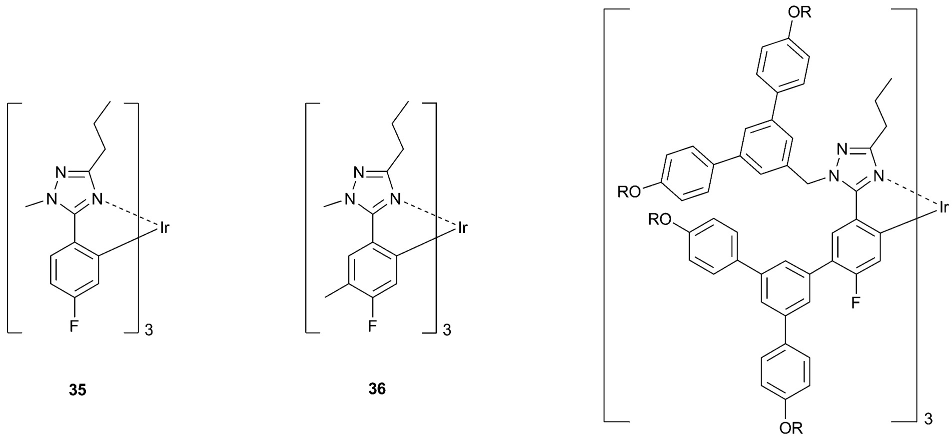
Scheme 1 *Conditions and reagents*: (i) Methyl-3,5-diiodobenzoate, $Pd(PPh_3)_4$, CuI, NEt_3, THF, heat, argon. (ii) 10% Pd/C, hydrogen, EtOAc, MeOH, r.t. (iii) Lithium aluminium hydride, THF, r.t. and then heat, argon. (iv) PBr_3, r.t. and then heat, argon. (v) Hydrazine monohydrate, EtOH, heat, argon. (vi) $CHCl_3$, r.t., argon. (vii) 3,5-Dibromoaldehyde, $Pd(PPh_3)_4$, CuI, NEt_3, THF, heat, argon. (viii) CBr_4, CH_2Cl_2, PPh_3, r.t., argon. (ix) Sodium *tert*-butoxide, toluene, heat, argon. (x) *tert*-Butyllithium, THF, −78 °C, argon, and then water, −78 °C to r.t, argon. (xi) $Pd(PPh_3)_4$, CuI, NEt_3, THF, heat, argon. (xii) 10% Pd/C, hydrogen, EtOAc, MeOH, r.t. (xiii) Iridium(III) chloride trihydrate, water, 2-(*n*-butoxy)ethanol, heat, argon, and then silver trifluoromethanesulfonate, **14**, heat, argon.

The first step in the preparation of dendrimer **34** with the 2-ethylhexyloxy surface groups was the synthesis of phenylacetylene **18**. 2-(2-Ethylhexyloxy)-4-iodobenzene **16**[33] was reacted with 2-methylbuty-3-yn-2-ol to give 4-[4-(2-ethylhexyloxy)phenyl]-2-methylbut-3-yn-2-ol **17** in quantitative yield under the standard Sonogashira coupling conditions. **17** was



Scheme 2 *Conditions and reagents*: (i) 2-Methylbut-3-yn-2-ol, $Pd(PPh_3)_4$, CuI, NEt_3, THF, heat, argon. (ii) Sodium *tert*-butoxide, heptane, heat, argon. (iii) 3,5-Dibromobenzaldehyde, $Pd(PPh_3)_4$, CuI, NEt_3, THF, heat, argon. (iv) CBr_4, CH_2Cl_2, PPh_3, r.t., argon. (v) Sodium *tert*-butoxide, toluene, heat, argon. (vi) *tert*-Butyllithium, THF, −78 °C, argon, and then water, −78 °C to r.t., argon. (vii) Methyl-4-fluoro-3-iodobenzoate, $Pd(PPh_3)_4$, CuI, NEt_3, THF, heat, argon. (viii) 10% Pd/C, hydrogen, EtOAc, MeOH, r.t. ix) Methyl-3,5-diiodobenzoate, $Pd(PPh_3)_4$, CuI, NEt_3, THF, heat, argon. (x) 10% Pd/C, hydrogen, EtOAc, MeOH, r.t. xi) Lithium aluminium hydride, THF, r.t. and then heat, argon. (xii) PBr_3, r.t. and then heat, argon. (xiii) Hydrazine monohydrate, EtOH, heat, argon. (xiv) LiOH, water, MeOH, THF, heat, argon and then 3 M $HCl_{(aq)}$, r.t. (xv) Thionyl chloride, heat, argon. (xvi) Ethyl butyrimidate hydrochloride, NEt_3, $CHCl_3$, argon. (xvii) **27**, $CHCl_3$, argon. (xviii) Iridium(III) chloride trihydrate, water, 2-(*n*-butoxy)ethanol, heat, argon, and then silver trifluoromethanesulfonate, **33**, heat, argon. R = 2-ethylhexyl.

then deprotected with sodium *tert*-butoxide to give after purification a 94% yield of **18**. To form the required dendron benzyl bromide precursor to the triazolyl ring, **18** was reacted with methyl-3,5-diiodobenzoate under Sonogashira conditions to give the first generation dendron **23** in a 97% yield. The acetylenes were then reduced using palladium on carbon catalysed



35

36

37 R = 2-ethylhexyl

Fig. 1 Structure of the parent **35** and methyl-substituted **36** complexes and first generation dendrimer **37** with 2-ethylhexyloxy surface groups and first generation biphenyl-based dendrons.

hydrogenation to give **24** also in a 97% yield. The ester at the focus of **24** was then reduced to the corresponding benzyl alcohol **25** with lithium aluminium hydride and then the benzyl alcohol **25** was converted into the benzylbromide **26** using phosphorous tribromide. This gave **26** in an overall yield of 93% for the two steps. For the preparation of the phenylacetylenyl-focussed dendron **22**, required for the formation of the dendronised ligand phenyl ring, **18** was first reacted with 3,5-dibromobenzaldehyde to give **19** in an 88% yield. The dibromovinyl focussed dendron **20** was then formed by reaction of **19** with triphenylphosphine and carbon tetrabromide in a 94% yield, and **20** was then converted to the bromoacetylene **21** in a 92% yield by treatment with sodium *tert*-butoxide in toluene at 50 °C. Finally the acetylene **22** was formed by metallation with *tert*-butyllithium followed by quenching of the anion in a 93% yield. The first generation acetylenyl focussed dendron **22** was then coupled with methyl-4-fluoro-3-iodobenzoate, which itself was prepared from 4-fluoro-3-iodotoluene by oxidation with potassium permanganate and then acid catalysed esterification with methanol in an overall yield of 44%. The Sonogashira coupling of dendron **22** with methyl-4-fluoro-3-iodobenzoate gave the dendronised phenyl ring of the ligand **28** in a quantitative yield. Hydrogenation of **28** afforded **29** with the saturated dendron in place in a 95% yield. The final formation of the doubly dendronised ligand involved several consecutive parallel steps. The ester of **29** was hydrolysed to give the corresponding acid **30**, which was then converted to the acid chloride **31** with thionyl chloride and subsequent reaction gave the butanimidic acid ethyl ester **32**. **32** was then reacted with the preformed benzylhydrazine **27** prepared by reaction of **26** with hydrazine hydrate to give 49% of the doubly dendronised ligand **33** as a single isomer. The final dendrimer **34** with the 2-ethylhexyloxy surface groups and two dendrons per ligand was synthesised using the two step sequence,[32] namely reaction with iridium(III) chloride trihydrate to form the chloro-bridged dimer followed by treatment of the dimer with an excess of **33** and silver trifluoromethanesulfonate. Under these conditions the dendrimer **34** was formed in a creditable 47% yield for the two steps. The proposed *facial* arrangement of **34** was consistent with the symmetry observed in the ^{1}H NMR spectrum.

We determined the hydrodynamic radii of the two new dendrimers using gel permeation chromatography (GPC) (against polystyrene standards) in combination with the Hester–Mitchell equation and Mark–Houwink relationship.[34] GPC analysis showed that dendrimers **15** and **34** were mono-disperse and had $\bar{M}_v$s of 1966 and 3836 corresponding to hydrodynamic radii of 9.4 Å and 13.8 Å, respectively. The presence of the 2-ethylhexyloxy surface groups clearly increases the relative size of the dendrimer. For comparison the doubly dendronised dendrimer **37** (Fig. 1) that has 2-ethylhexyloxy groups and first generation biphenyl-based dendrons has a hydrodynamic radius of 12.8 Å.[26] The larger radius of **34** with respect to **37** illustrates the fact that the ethylene linkers make the dendrons and hence dendrimers larger. It is interesting to note that **15**, which does not have any surface groups, was very soluble in a range of organic solvents including chloroform, toluene and tetrahydrofuran unlike the case of iridium(III) complex cored dendrimers with biphenyl dendrons but no surface groups.[35] The flexibility within the dendron and the link to the iridium(III) complex core clearly improves the solubility of dendrimers.

Given the difference in solubility between the dendrimers with the rigid and flexible dendrons, we were interested to see what affect the flexible dendrons had on the thermal properties of the dendrimers. Thermal gravimetric analysis of **15** and **34** showed that they had good thermal stability with both dendrimers having decomposition temperatures, corresponding to a 5% weight loss, of around 400 °C. Differential Scanning Calorimetry showed that **15** (without the surface groups) and **34** (with the surface groups) had glass transition temperatures (T_gs) of 34 °C and −3 °C, respectively. In contrast, **37** with the rigid biphenyl dendrons and the 2-ethylhexyloxy surface groups had a T_g of 76 °C. It is therefore clear that while the surface groups can play an important role in the processing of the dendrimers, they can also depress their thermal transitions. The fact that the T_g of **37** is higher than **15** or **34** indicates that a reduction in the T_g can be counteracted, at least in part, by using rigid structures in the dendrons. Therefore, the balance between rigid and flexible units within a light-emitting dendrimer structure is an important design criterion.

Photophysical and electronic properties

To understand the effect of the 1,2-diphenylethylene dendrons on the properties of the emissive core, we compare the properties of dendrimers **15** and **34** with a simple parent complex **35**, the methyl-substituted complex **36**,[25] and doubly dendronised biphenyl dendrimer **37** (Fig. 1).[26] The UV-visible absorption spectra of dendrimers **15** and **34** are shown in Fig. 2. The stronger absorptions at short wavelength (240–320 nm) correspond to the π–π^* transitions of the ligands with those at wavelengths >320 nm being due to a transition between a Highest Occupied Molecular Orbital consisting of metal d orbitals and ligand π orbitals and a Lowest Unoccupied Molecular Orbital mainly consisting of ligand π orbitals.[18] The onset of absorption of the dendrimers is slightly red-shifted compared to the simple core complex **35** and this is due to the presence of the alkyl group attached to the phenyl ring of the ligand. Evidence for this comes from the absorption of the methyl substituted complex **36**, which has the same onset to absorption. The next step in the analysis of the photophysical properties was the measurement of the solution photoluminescence (PL) spectra (at room temperature, Fig. 3). It can be seen that as with the absorption spectrum the addition of the methyl group shifts the PL spectrum of **36** to the red when compared with the core complex **35**. The dendrons and/or the presence of the surface groups do not change the positions of the peaks appreciably when compared to **36** (see Table 1) and the dendrimers emit deep blue light with Commission Internationale de l'Eclairage (CIE) co-ordinates of (0.15–0.16, 0.14–0.18). The CIE co-ordinates are slightly different for each of the compounds due to a different weighting of the (0,0) and (0,1) transitions. On moving to the solid state the PL spectra of dendrimers **15** and **34** were essentially the same even though there was a small red-tail in the film PL of **15** (Fig. 4). The similarity in the PL spectra on going from solution to film indicates that to a first approximation the dendrons are controlling the intermolecular interactions that lead to the quenching of the luminescence.

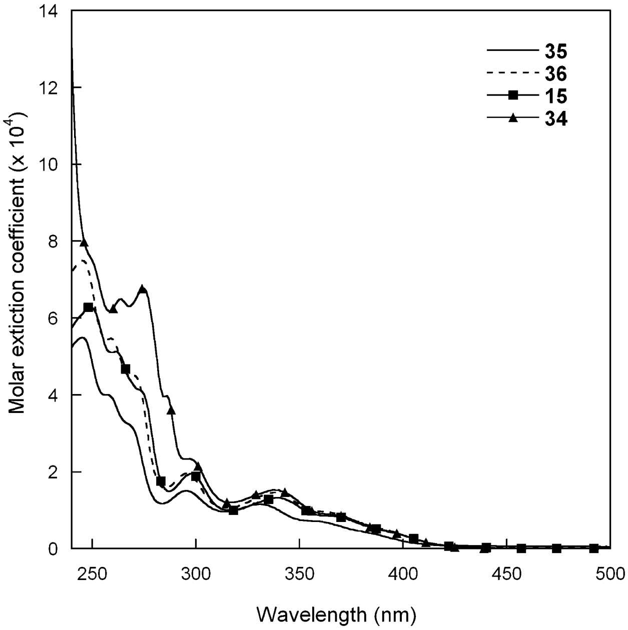


Fig. 2 Solution (dichloromethane) UV-visible spectra for **15**, **34**, **35**, and **36**.

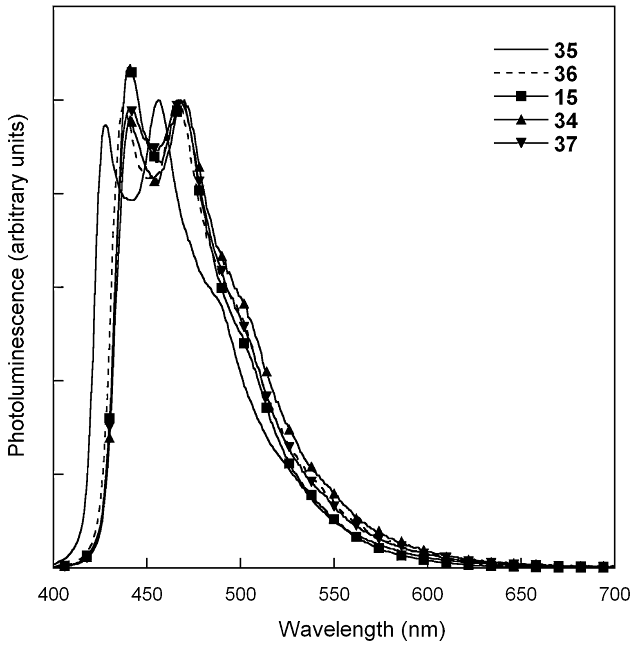


Fig. 3 Solution (toluene) PL spectra of **15**, **34**, **35**, **36**, and **37**. The spectra have been normalised for ease of comparison.

Table 1 Summary of the photophysical and electrochemical properties of the iridium(III) complexes and dendrimers

	PL		PLQYs (%)		PL lifetime[a]	
	peaks [nm][a]	CIEs (x,y)[a]	Solution[a]	Film[b]	τ [µs]	$E_{1/2}$ (ox)[c] [V]
35[18]	428, 456	(0.16, 0.13)	27	—	1.25	0.50
36[25]	437, 467	(0.16, 0.16)	40	—	1.93	0.41
37[26]	441, 468	(0.15, 0.16)	59	17	22	0.53
15	441, 468	(0.15, 0.14)	46	21	1.72	0.47
34	441, 470	(0.16, 0.18)	45	49	1.65	0.45

[a] Measured in toluene. [b] Spin-coated from chloroform solution. [c] The potentials are quoted against the ferricenium/ferrocene couple, scan rate = 40 mV/s, solvent = dichloromethane, concentration = 1 mM, platinum working electrode.

To understand the effect of the dendrons on the photophysical properties of the emissive iridium(III) complex core in greater detail, we measured the solution PLQYs and time resolved PL (TRPL) (Table 1). The first point to note is that the solution PLQYs of **15** and **34** are significantly higher than the parent complex **35** and essentially the same as each other. Compound **36** has a similar solution PLQY, showing that the addition of the alkyl groups significantly increases the luminescence of the complexes, whilst only slightly changing the colour. The solution PLQYs of the dendrimers with the diphenylethylene dendrons are slightly lower than that of **37**, which has the biphenyl dendrons. However, the PL lifetimes of **15** and **34** are shorter by more than an order of magnitude when compared to that of the **37** and close to that of the core complex (Table 1). This indicates

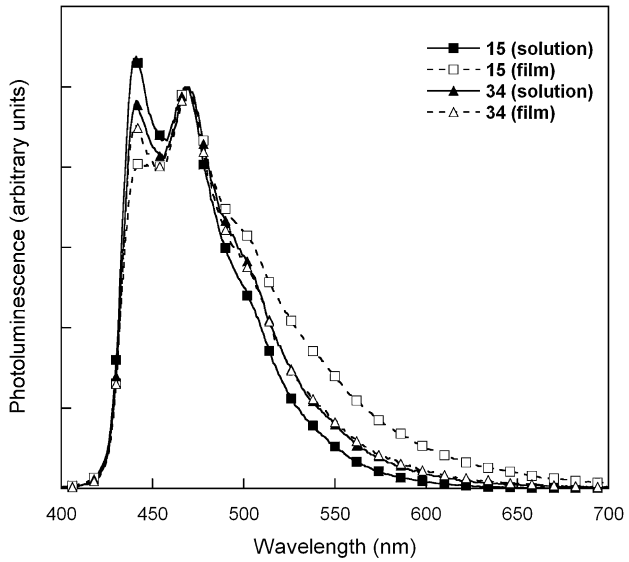


Fig. 4 Solution (toluene) and film PL spectra of **15** and **34**. The spectra have been normalised for ease of comparison.

that the strong modification of the luminescence process in **37**, which is due to the triplet spending time on the dendron, has been avoided in **15** and **34** by the high triplet energy dendrons. That is, for **15** and **34** the triplet is localised on core metal complex, whereas for **37** it also spends time on the dendrons. Finally, the film PLQYs of the dendrimers were measured. For dendrimer **37** with the biphenyl dendrons there was a significant drop in the PLQY in moving from solution to the solid state (from 59% to 17%).[26] Intermolecular interactions of emissive chromophores can lead to the quenching of the luminescence and while the core of dendrimer **37** is surrounded by dendrons and surface groups, the triplet excitons spend time on the dendron of **37** and hence dendron–dendron interactions can also lead to quenching of the luminescence. For dendrimer **15** (without the surface groups) there was a 50% decrease in the PLQY in moving from solution to the solid state. However, for dendrimer **34** with surface groups the solution and solid state PLQYs were essentially the same, with an excellent solid state PLQY of 49% for an emission colour with CIE co-ordinates of (0.16, 0.18). The lower solid state PLQY for dendrimer **15** indicates that the lack of surface groups allows an increase of intermolecular interactions of the emissive core. That is, the surface groups not only play an important role in the processing of the dendrimers but also in the way the emissive cores interact in the solid state.

A final aspect of the study was to determine the effect of the dendrons on the electronic properties of the dendrimers. Cyclic voltammetry measurements were carried out on dendrimers **15** and **34** and the methyl substituted core. Under the conditions used we were able to observe a single chemically reversible oxidation for each of the materials and the results are summarised in Table 1. However, we could not observe chemically reversible reductions under the conditions used. The first key point to note is that the electroactive component of dendrimers **15** and **34** is the core. This can be seen by the fact that the oxidation potential does not change appreciably for **15** and **34** when compared with the methyl substituted complex **36**. Indeed the oxidation potentials of all the materials are similar indicating that attachment of a dendron *para* to the iridium and *meta* to the heterocyclic ring has little effect on the highest occupied molecular orbital energies.

Conclusions

In conclusion we have developed methodology for forming diphenylethylene-based dendrons. These dendrons are like Fréchet dendrons in that the branching points are separated by saturated units but are without the relatively sensitive benzyloxy group. Such dendrons could therefore be of use in applications in which the benzyloxy group is unstable. The diphenylethylene-based dendrons have a high triplet energy making them suitable for encapsulating deep blue emissive iridium(III) complexes. The diphenylethylene dendrons were found not to quench the luminescence of the emissive core in solution, and enhanced the solution PLQY of the core chromophore. In the solid state it was found that the combination of dendrons and surface groups enabled a high room temperature PLQY (49%) for a neat spin-coated film of a blue phosphorescent material to be achieved. Our results show that high triplet energy dendrons are required for blue phosphorescent dendrimers.

Experimental

Synthesis of organic materials

Unless otherwise noted, all chemicals were obtained from commercial suppliers and used as received. Melting points were measured in a glass capillary on a Gallenkamp melting point apparatus and are uncorrected. The ^{1}H NMR spectra were measured in deuterated chloroform with either Bruker DPX 400 MHz, DQX 400 MHz, or AMX 500 MHz spectrometers: SP = surface phenyl; BP = branch phenyl; LP = ligand phenyl; EH = 2-ethylhexyl; Pr = *n*-propyl. All *J* values are rounded to the nearest 0.5 Hz. Microanalyses were carried out in the Inorganic Chemistry Laboratory, Oxford, or at the Metropolitan University, London, UK. The UV-visible absorption spectra were recorded as solutions in HPLC grade dichloromethane with a Perkin-Elmer UV-vis Lambda 25 spectrometer. Mass spectra were recorded on a Waters LCT Premier XE for TOF ES or an Applied Biosystems Voyager matrix-assisted laser desorption/ionisation time-of-flight (MALDI-TOF) from 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile, (DCTB) in positive reflection mode at the EPSRC National Mass Spectrometry Centre, Swansea, UK or a Micromass Tofspec E spectrometer matrix-assisted laser desorption/ionisation time-of-flight (MALDI-TOF) from 2-5-dihydroxybenzoic acid, (DHB) in positive reflection mode at Oxford. Thermal gravimetric analysis was performed on a Perkin-Elmer thermogravimetric analyzer TGA7. Differential Scanning Calorimetry was carried out using a Perkin Elmer Pyris 1. Gel permeation chromatography was carried out using PLgel Mixed-A columns (600 mm + 300 mm lengths, 7.5 mm diameter) from Polymer Laboratories calibrated with polystyrene narrow standards ($\bar{M}p$ = 580 to 3.2 $\times$ 10^{6}) in tetrahydrofuran. The tetrahydrofuran was degassed with helium and pumped with a rate of 1 mL/min at 30.0 °C. Light petroleum refers to the fraction of boiling point 40–60 °C.

When solvent mixtures are used for chromatography over silica, the proportions are given by volume.

Electrochemical measurements

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 dichloromethane, with 0.1 M tetra-ethylammonium tetrafluoroborate as the electrolyte. The electrolyte was purified by recrystallization from a mixture of ethyl acetate and diethyl ether. The solutions were deoxygenated with argon. The ferricenium/ferrocene couple was used as standard[36] and the ferrocene was purified by sublimation. All potentials are quoted relative to the ferricenium/ferrocene couple. In all cases several scans were carried out to confirm the chemical reversibility of the redox processes.

Photophysical studies

For solution measurements samples were dissolved in spectroscopic grade toluene, their optical density was adjusted to 0.1 ± 0.01 at 360 nm. The solution was transferred into quartz degassing cuvettes, then degassed by three freeze–pump–thaw cycles, sealed under vacuum, and warmed to nominal room temperature in a bath of water. A Jobin Yvon Fluoromax 2 fluorimeter was used to measure the photoluminescence spectra. The measurements in solution were recorded using, the highest spectral resolution, using an excitation wavelength of 360 nm, whilst those in film were recorded using a medium resolution at an excitation wavelength of 325 nm. Spectra were corrected after measurement using the emission calibration obtained from measuring a calibrated lamp spectrum. Solution PLQYs were measured by a relative method using quinine sulfate in 0.5 M sulfuric acid as a standard.[37] The error in this method is estimated to be approximately 10%. Film PLQYs were measured by exciting with a HeCd laser at a wavelength of 325 nm using a calibrated integrating sphere.[38]

Photoluminescence lifetimes were measured on the same degassed solutions at room temperature by the method of time-correlated single-photon counting (TCSPC). The samples were excited at 390 nm by a pulsed light-emitting diode (Picoquant PLS 370) giving 10 pJ/pulse at a pulse repetition rate of 100 kHz. The emission was focused onto a monochromator entrance slit and detected with a cooled Hamamtsu micro-channel plate photomultiplier tube RU-3809U-50. The average number of photons collected per pulse was 0.1 or less. The apparatus response function was ≈0.5 ns (FWHM) in the shortest time window. The measured lifetime was obtained by fitting a single exponential decay to the measured transient.

Methyl-3,5-bis[2-phenylacetylen-1-yl]benzoate 2. Tetrakis-(triphenylphosphine)palladium(0) (83 mg, 0.07 mmol) was added to a deoxygenated (by placing under vacuum and backfilling with argon) mixture of methyl-3,5-diiodobenzoate (400 mg, 1.03 mmol), phenylacetylene **1** (316 mg, 3.09 mmol), copper iodide (30 mg, 0.14 mmol), triethylamine (3 cm^3), and tetrahydrofuran (3 cm^3). The mixture was deoxygenated again and then heated in an oil bath held at 60 °C under argon for 18 h. The mixture was cooled to room temperature and the solvents were removed. Water (16 cm^3) was added and the mixture was extracted with dichloromethane (4 × 10 cm^3). The dichloromethane extracts were combined, washed with brine (20 cm^3), dried over anhydrous sodium sulfate and filtered. The filtrate was collected and the solvent was removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (1:70 to 1:3) mixtures as eluent to give **2** as a light yellow solid (346 mg, 99%); mp 105–106 °C; (Found: C, 85.6; H, 4.7. $C_{24}H_{16}O_2$ requires C, 85.7; H, 4.8%); λ_{max} (CH_2Cl_2)/nm: 259 sh (log ε/dm^3 mol^{-1} cm^{-1} 4.69), 271 sh (4.81), 285 (4.95), 290 sh (4.91), 302 (4.92) and 336 sh (3.69); ν_{max} (film)/cm^{-1} 1728 (C=O), 2214 (C≡C); δ_H (400.1 MHz, $CDCl_3$) 3.97 (3 H, s, $COOCH_3$), 7.36–7.40 (6 H, m, SP H), 7.52–7.58 (4 H, m, SP H), 7.87 (1 H, dd *J* 1.5, *J* 1.5, G1-BP H) and 8.16 (2 H, d, *J* 1.5, G1-BP H); δ_C (100.6 MHz; $CDCl_3$) 52.4, 87.6, 90.85, 122.6, 124.1, 128.4, 128.7, 130.8, 131.7, 132.1, 138.2 and 165.8; *m*/*z* [microTOF ES$^+$] 337.1 (MH^+), 359.1 (M^+ + Na).

Methyl-3,5-bis[2-phenylethylen-1-yl]benzoate 3. A solution of **2** (403 mg, 1.20 mmol), ethyl acetate (23 cm^3), and methanol (23 cm^3) was deoxygenated (by placing under vacuum and backfilling with argon) four times. 10% Palladium on carbon (102 mg) was added to the mixture and the mixture was deoxygenated three times. A balloon filled with hydrogen was attached and the reaction mixture was briefly degassed and backfilled with hydrogen three times. The reaction was stirred at room temperature under hydrogen for 17 h. The mixture was passed through a plug of silica using dichloromethane as eluent (the silica was poured into excess water immediately to quench the catalyst). The filtrate was collected and the solvent was removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (0:1 to 1:5) mixtures as eluent to give **3** as a colourless oil (360 mg, 87%); (Found: C, 83.7; H, 7.1. $C_{24}H_{24}O_2$ requires C, 83.7; H, 7.0%); λ_{max} (CH_2Cl_2)/nm: 238 (log ε/dm^3 mol^{-1} cm^{-1} 4.03), 269 (3.12), 285 (3.28) and 293 (3.24); ν_{max} (neat)/cm^{-1} 1722 (C=O); δ_H (400.1 MHz, $CDCl_3$) 2.92 (8 H, m, CH_2CH_2), 3.93 (3 H, s, $COOCH_3$), 7.09 (1 H, s, G1-BP H), 7.15–7.24 (6 H, m, SP H), 7.27–7.33 (4 H, m, SP H) and 7.74 (2 H, s, G1-BP H); δ_C (100.6 MHz; $CDCl_3$) 37.7, 37.8, 52.05, 126.0, 127.3, 128.4, 128.5, 130.2, 133.6, 141.4, 142.0 and 167.4; *m*/*z* [TOF ES$^+$] 345.3 (MH^+), 362.3 (MNH_4^+).

3,5-Bis[2-phenylethylen-1-yl]benzyl alcohol 4. Lithium aluminium hydride (144 mg, 3.80 mmol) was added to a solution of **3** (600 mg, 1.74 mmol) in anhydrous tetrahydrofuran (29 cm^3). The mixture was stirred at room temperature for 5 min and then heated in an oil bath held at 60 °C under argon for 4 h. The reaction was allowed to cool to room temperature and carefully poured into a mixture of ice and water (≈20 cm^3). The mixture was extracted with ethyl acetate (4 × 20 cm^3). The ethyl acetate extracts were combined, washed with brine (30 cm^3), dried over anhydrous sodium sulfate, and filtered. The filtrate was collected and the solvent was removed to give **4** as a colourless oil (537 mg, 97%); (Found: C, 87.2; H, 7.75. $C_{23}H_{24}O_2$ requires C, 87.3; H, 7.6%); λ_{max} (CH_2Cl_2)/nm: 248 sh (log ε/dm^3 mol^{-1} cm^{-1} 2.83), 254 sh (2.94), 259 (2.99), 263 sh (2.96), 269 (2.91), 274 sh (2.56) and 293 sh (1.97); ν_{max} (neat)/cm^{-1} 3326 (OH); δ_H (400.1 MHz,

$CDCl_3$) 1.58 (1 H, s, OH), 2.90 (8 H, s, CH_2CH_2), 4.65 (2 H, d, *J* 4.5, $ArCH_2O$), 6.93 (1 H, s, G1-BP H), 7.03 (2 H, s, G1-BP H), 7.17–7.24 (6 H, m, SP H) and 7.27–7.33 (4 H, m, SP H); δ_C (100.6 MHz, $CDCl_3$) 37.8, 37.9, 65.2, 124.7, 125.9, 128.0, 128.3, 128.4, 140.9, 141.7 and 142.0; *m/z* [microTOF ES^+] 339.2 (M^+ + Na).

3,5-Bis[2-phenylethylen-1-yl]benzylbromide 5. Phosphorus tribromide (0.7 cm^3, 7.57 mmol) was added to **4** (537 mg, 1.70 mmol) with care. The mixture was heated in an oil bath held at 93 °C under argon for 14 h. The reaction was cooled to room temperature and diluted with ether (15 cm^3). The mixture was cooled to 0–2 °C and very carefully quenched with a mixture of ice and water (10 cm^3). The two layers were separated and the aqueous layer was extracted with ether (3 × 10 cm^3). The organic layers were combined, washed with brine (20 cm^3), dried over anhydrous sodium sulfate, and filtered. The filtrate was collected and the solvent was removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (1:40 to 1:5) mixtures as eluent to give **5** as a colourless oil (640 mg, 99%); (Found: C, 72.9; H, 6.1. $C_{23}H_{23}Br$ requires C, 72.8; H, 6.1%); λ_{max} (CH_2Cl_2)/nm: 241 sh (log ε/dm^3 mol^{-1} cm^{-1} 3.90), 269 sh (3.23) and 283 sh (2.87); δ_H (400.1 MHz, $CDCl_3$) 2.89 (8 H, s, CH_2CH_2), 4.46 (2 H, s, $ArCH_2Br$), 6.91 (1 H, s, G1-BP H), 7.05 (2 H, s, G1-BP H), 7.16–7.24 (6 H, m, SP H) and 7.27–7.33 (4 H, m, SP H); δ_C (100.6 MHz, $CDCl_3$) 33.8, 37.7, 37.8, 125.9, 126.8, 128.3, 128.4, 129.0, 137.7, 141.5 and 142.3; *m/z* [microTOF ES^+] 403.1 (M^+ + Na).

3,5-Bis[2-phenylacetylen-1-yl]benzaldehyde 9. A mixture of 3,5-dibromobenzaldehyde (4.33 g, 16.4 mmol), phenylacetylene **1** (4.20 g, 41.1 mmol), copper iodide (330 mg, 1.73 mmol), triethylamine (40 cm^3), and tetrahydrofuran (40 cm^3) was deoxygenated (by placing under vacuum and backfilling with argon) four times. Tetrakis(triphenylphosphine)palladium(0) (1.00 g, 0.865 mmol) was added to the mixture, which was then deoxygenated further four times. The solution was heated under argon in an oil bath held at 76 °C for 63 h. The reaction was cooled to room temperature and the solvent was removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (1:100 to 1:5) mixtures as eluent to give **9** as a brownish solid (4.08 g, 81%); mp 85–88 °C; (Found: C, 90.1; H, 4.5. $C_{24}H_{13}O$ requires C, 90.2; H, 4.6%); λ_{max} (CH_2Cl_2)/nm: 277 sh (log ε/dm^3 mol^{-1} cm^{-1} 5.00), 285 (5.06), 303 (4.98) and 341 sh (3.87); ν_{max} (film)/cm^{-1} 1704 (C=O), 2212 (C≡C); δ_H (400.1 MHz, $CDCl_3$) 7.33–7.47 (6 H, m, SP H), 7.52–7.63 (4 H, m, SP H), 7.94 (1 H, dd, *J* 1.5, *J* 1.5, G1-BP H), 7.98 (1 H, d, *J* 1.5, G1-BP H) and 10.02 (1 H, s, CHO); δ_C (100.6 MHz; $CDCl_3$) 87.2, 91.5, 122.4, 124.9, 128.5, 128.9, 131.7, 131.9, 136.6, 139.5 and 190.9.

1-[3,5-Bis(2-phenylacetylen-1-yl)phenyl]-2,2-dibromovinylene 10. A solution of **9** (4.00 g, 13.1 mmol), carbon tetrabromide (8.66 g, 26.1 mmol) and dichloromethane (70 cm^3) was cooled in a water bath. Triphenylphosphine (13.7 g, 52.2 mmol) was added in portions over a period of 7 min to the mixture (Note: the reaction is exothermic). After addition of the triphenylphosphine, the water bath was removed and the reaction was stirred at room temperature under argon for 14 h. The solvent was removed and the residue was purified by column chromatography over silica using dichloromethane:light petroleum (1:10 to 1:5) mixtures as eluent to give **10** as a brownish oil (5.42 g, 90%); (Found: C, 62.4; H, 3.1; $C_{24}H_{14}Br_2$ requires C, 62.4; H, 3.05%); λ_{max} (CH_2Cl_2)/nm: 272 sh (log ε/dm^3 mol^{-1} cm^{-1} 5.29), 280 sh (5.34), 287 (5.40) and 304 (5.30); ν_{max} (neat)/cm^{-1} 2213 (C≡C); δ_H (400.1 MHz, $CDCl_3$) 7.37–7.44 (6 H, m, SP H), 7.46 (1 H, s, Br_2C=CH), 7.53–7.60 (4 H, m, SP H), 7.64 (2 H, d, *J* 1.5, G1-BP H) and 7.68 (1 H, dd, *J* 1.5, *J* 1.5, G1-BP H); δ_C (100.6 MHz; $CDCl_3$) 87.9, 90.5, 91.7, 122.7, 124.0, 128.4, 128.6, 130.9, 131.7, 134.3, 135.3 and 135.9.

1-[3,5-Bis(2-phenylacetylen-1-yl)phenyl]-2-bromoacetylene 11. Sodium *tert*-butoxide (2.26 g, 23.5 mmol) was added to a solution of **10** (5.42 g, 11.7 mmol) in toluene (167 cm^3). The mixture was heated in an oil bath at 50 °C under argon for 15 h. The reaction was cooled to room temperature and the solvent was removed. Water (10 cm^3) was added to the residue and the mixture was extracted with dichloromethane (3 × 20 cm^3). The organic layers were combined, washed with brine (20 cm^3), dried over sodium sulfate, and filtered. The filtrate was collected and the solvent removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (1:30 to 1:5) mixtures as eluent to give **11** as a white solid (4.32 g, 97%); mp 103–104 °C; (Found: C, 75.7; H, 3.4. $C_{24}H_{13}Br$ requires C, 75.6; H, 3.4%); λ_{max} (CH_2Cl_2)/nm: 243sh (log ε/dm^3 mol^{-1} cm^{-1} 4.43), 269 (4.69), 279 sh (4.67), 286 (4.77), 293 sh (4.70) and 304 (4.75); ν_{max} (film)/cm^{-1} 2185 (C≡C), 2211 (C≡C); δ_H (400.1 MHz, $CDCl_3$) 7.33–7.40 (6 H, m, SP H), 7.50–7.60 (6 H, m, SP H & G1-BP H) and 7.67 (1 H, dd, *J*, 1.5, *J* 1.5, G1-BP H); δ_C (100.6 MHz; $CDCl_3$) 51.4, 78.6, 87.6, 90.7, 122.7, 123.4, 124.1, 128.4, 128.7, 131.7, 134.4 and 134.5; *m/z* [TOF FI^+] 380.0, 382.0 (M^+).

1-[3,5-Bis(2-phenylacetylen-1-yl)phenyl]acetylene 12. A solution of **11** (4.32 g, 11.3 mmol) in tetrahydrofuran (180 cm^3) was cooled to −78 °C under argon. *Tert*-butyllithium (10.7 cm^3, 18.1 mmol) was added dropwise with care to the mixture. The reaction was stirred at −78 °C for 2 h and then water (20 cm^3) was added *very carefully while the mixture was at −78 °C.* The reaction was allowed to warm to room temperature and then stirred for 13 h. The tetrahydrofuran was removed and the residue was extracted with dichloromethane (4 × 20 cm^3), and the combined extracts were washed with brine (25 cm^3), dried over magnesium sulfate, and filtered. The filtrate was collected and the solvent was removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (1:20 to 1:10) mixtures as eluent to give **12** as a white solid (3.15 g, 92%); mp 83–84 °C; (Found: C, 95.2; H, 4.6. $C_{24}H_{14}$ requires C, 95.3; H, 4.7%); λ_{max} (CH_2Cl_2)/nm: 244 sh (log ε/dm^3 mol^{-1} cm^{-1} 4.63), 257 (4.73), 272 sh (4.78), 279 sh (4.84), 286 (4.95), 293 sh (4.88) and 303 (4.94); ν_{max} (film)/cm^{-1} 2211 (C≡C), 3292 (C≡C–H); δ_H (400.1 MHz, $CDCl_3$) 3.13 (1 H, s, C≡C–H), 7.35–7.40 (6 H, m, SP H), 7.50–7.58 (4 H, m, SP H), 7.61 (2 H, d, *J* 1.5, G1-BP H) and 7.69 (1 H, dd, *J* 1.5, *J* 1.5, G1-BP H); δ_C (100.6 MHz; $CDCl_3$) 78.3, 82.0, 87.6, 90.6, 122.7, 122.8, 124.0, 128.4, 128.6, 131.7, 134.5 and 134.6; *m/z* [EI^+] Anal. Calcd for $C_{24}H_{14}$: 302.1096 (M^+). Found: 302.1090 (M^+).

1-[3,5-Bis(2-phenylethylen-1-yl)benzyl]-5-(4-fluoro-3-iodophenyl)-3-*n*-propyl-1*H*-1,2,4-triazole 8. **5** (520 mg, 1.37 mmol) was added slowly to a solution of hydrazine monohydrate (360 mg, 7.32 mmol) in ethanol (10 cm^3) heated at reflux. After addition, the mixture was kept at reflux under argon for 14 h. The reaction was allowed to cool to room temperature and the solvent was removed. The residue was dissolved in dichloromethane (40 cm^3), dried over anhydrous sodium sulfate, and filtered. The filtrate was collected and the solvent was removed to give a colourless oil of **6** ($\approx$453 mg), which was used without purification. A mixture of thionyl chloride (2.1 cm^3) and 4-fluoro-3-iodobenzoic acid (1.98 g, 7.44 mmol) was heated at reflux for 27 h under argon. The reaction was allowed to cool and the excess thionyl chloride was removed to give *4-fluoro-3-iodobenzoyl chloride* ($\approx$1.97 g) as a light brown solid. Triethylamine (0.5 cm^3) was added dropwise to a mixture of 4-fluoro-3-iodobenzoyl chloride ($\approx$390 mg, $\approx$1.37 mmol), ethyl butyrimidate hydrochloride (208 mg, 1.37 mmol) and dichloromethane (9 cm^3) under argon. The reaction mixture was stirred at room temperature for 15 h. The mixture was washed with water (4 × 7 cm^3) and brine (7 cm^3), dried over anhydrous sodium sulfate, and filtered. The filtrate was collected and the solvent was removed to give a brownish oil of the ethyl butyrimidate ester **7** ($\approx$498 mg), which was used without purification. A solution of **6** ($\approx$453 mg) in chloroform (2 cm^3) was added to a solution of **7** ($\approx$498 mg) in chloroform (8 cm^3) under argon. The reaction mixture was stirred at room temperature for 22 h. The solvent was removed to leave a yellow oil as the residue. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (1:10 to 1:0) and ethyl acetate–dichloromethane (1:10) mixtures as eluent to give **8** as a colourless oil (556 mg, 64% for the two steps with respect to **5**); (Found: C, 65.0; H, 5.2; N, 6.6. $C_{34}H_{33}FIN_3$ requires C, 64.9; H, 5.3; N, 6.7%); λ_{max} (CH_2Cl_2)/nm: 253 sh (log ε/dm^3 mol^{-1} cm^{-1} 3.94) and 310 sh (2.93); δ_H (400.2 MHz, $CDCl_3$) 1.04 (3 H, t, *J* 7.5, Pr CH_3), 1.85 (2 H, m, Pr CH_2), 2.73 (2 H, t, *J* 7.5, Pr CH_2), 2.86 (8 H, s, CH_2CH_2), 5.27 (2 H, s, NCH_2Ar), 6.81 (2 H, s, G1-BP H), 6.91 (1 H, s, G1-BP H), 7.06–7.29 (11 H, m, SP H & LP H), 7.46 (1 H, m, LP H) and 7.94 (1 H, dd, *J* 2 & 6, LP H); δ_F (376.6 MHz, $CDCl_3$) −91.0; *m*/*z* [microTOF ES$^+$] 630.2 (MH$^+$).

1-[3,5-Bis(2-phenylethylen-1-yl)benzyl]-5-[4-fluoro-3-(2-{3,5-bis-[2-phenylacetylen-1-yl]phenyl}acetylen-1-yl)phenyl-3-*n*-propyl-1*H*-1,2,4-triazole 13. A mixture of **8** (470 mg, 0.75 mmol), **12** (270 mg, 0.90 mmol), copper iodide (37 mg, 0.19 mmol), triethylamine (3.7 cm^3) and tetrahydrofuran (3.7 cm^3) was deoxygenated (by placing under vacuum and backfilling with argon) four times. Tetrakis(triphenylphosphine)palladium(0) (60 mg, 0.05 mmol) was added to the mixture, which was then deoxygenated further four times. The reaction mixture was heated under argon in an oil bath held at 77 °C for 15 h. The reaction was cooled to room temperature and the solvents were removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (1:20 to 1:0) mixtures as eluent to give **13** as a colourless oil (476 mg, 79%); (Found: C, 88.7; H, 5.7; N, 5.3. $C_{58}H_{46}FN_3$ requires C, 88.6; H, 5.8; N, 5.2%); λ_{max} (CH_2Cl_2)/nm: 258 sh (log ε/dm^3 mol^{-1} cm^{-1} 4.25), 273 sh (4.40), 288 (4.58), 296 sh (4.51) and 305 (4.56); ν_{max} (neat)/cm^{-1} 2214 (C≡C); δ_H (400.2 MHz, $CDCl_3$) 1.06 (3 H, t, *J* 7.5, Pr CH_3), 1.88 (2 H, m, Pr CH_2), 2.77–2.88 (10 H, m, Pr CH_2 & CH_2CH_2), 5.32 (2 H, s, NCH_2Ar), 6.79 (2 H, s, G1-BP H), 6.90 (1 H, s, G1-BP H), 7.10 (4 H, m, SP H), 7,14–7.20 (3 H, m, SP H & LP H), 7.24 (4 H m, SP H),7.39 (6 H, m, SP H), 7.47 (1 H, m, LP H), 7.56 (4 H, m, SP H), 7.62 (2 H, d, *J* 1.5, G1-BP H), 7.68 (1 H, dd, *J* 1.5, *J* 1.5, G1-BP H) and 7.72 (1 H, dd, *J* 2, *J* 6.5, LP H); δ_F (376.6 MHz, $CDCl_3$) −106.9; *m*/*z* [TOF ES$^+$] 804.3 (MH$^+$).

1-[3,5-Bis(2-phenylethylen-1-yl)benzyl]-5-[4-fluoro-3-(2-{3,5-bis-[2-phenylethylen-1-yl]phenyl}ethylen-1-yl)phenyl]-3-*n*-propyl-1*H*-1,2,4-triazole 14. A solution of **13** (470 mg, 0.58 mmol) in an ethyl acetate (8.5 cm^3) and methanol (15 cm^3) mixture was deoxygenated (by placing under vacuum and backfilling with argon) four times. 10% Palladium on carbon (66 mg) was added to the solution and the mixture was degassed then deoxygenated further four times. A balloon filled with hydrogen was attached and the mixture was briefly degassed and backfilled with hydrogen four times. The reaction mixture was stirred at room temperature under an atmosphere of hydrogen for 16 h. The mixture was passed through a plug of silica using dichloromethane as eluent (the silica was poured into excess water immediately to quench the catalyst). The filtrate was collected and the solvent removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (1:40 to 1:3) mixtures as eluent to give **14** as a light yellow oil (409 mg, 86%); (Found: C, 85.4; H, 7.1; N, 5.25. $C_{58}H_{58}FN_3$ requires C, 85.4; H, 7.2; N, 5.15%); λ_{max} (CH_2Cl_2)/nm: 247 sh (log ε/dm^3 mol^{-1} cm^{-1} 4.16); δ_H (400.1 MHz, $CDCl_3$) 1.04 (3 H, t, *J* 7.5, Pr CH_3), 1.86 (2 H, m, Pr CH_2), 2.75–2.92 (22 H, m, Pr CH_2 & CH_2CH_2), 5.21 (2 H, s, NCH_2Ar), 6.74 (2 H, s, G1-BP H), 6.80 (3 H, bm, G1-BP H), 6.88 (1 H, s, G1-BP H), 7.04–7.34 (22 H, m, SP H & LP H) and 7.43 (1 H, dd, *J* 2, *J* 7, LP H); δ_F (376.6 MHz, $CDCl_3$) −115.6; *m*/*z* [microTOF ES$^+$] 816.5 (MH$^+$).

Tris-*fac*-[1-(3,5-bis{2-phenylethylen-1-yl}benzyl)-5-(4-fluoro-3-{2-[3,5-bis(2-phenylethylen-1-yl)phenyl]ethylen-1-yl}phenyl)-3-*n*-propyl-1*H*-1,2,4-triazolyl]iridium(III) 15. A mixture of **14** (240 mg, 0.29 mmol), iridium(III) chloride trihydrate (43 mg, 0.12 mmol), water (0.5 cm^3), and 2-(*n*-butoxy)ethanol (1.5 cm^3) was heated at reflux under argon for 14 h. The reaction was allowed to cool to room temperature to leave a brown gel and a yellow liquid. The liquid was removed and the gel was triturated with water (3 × 2 cm^3). The residue was dissolved in dichloromethane (10 cm^3), dried over anhydrous sodium sulfate and filtered. The filtrate was collected and the solvent was removed to give a brown–yellow oil (270 mg) containing a mixture of the iridium chloro-bridged dimer and **14**. A mixture of the oil (270 mg), **14** (560 mg, 0.69 mmol), silver trifluoromethanesulfonate (63 mg, 0.24 mmol) was heated under argon in an oil bath held at 166 °C for 14.5 h. The mixture was allowed to cool to room temperature and then purified by column chromatography over silica using dichloromethane:light petroleum (1:20 to 2:1) and ethyl acetate:dichloromethane (1:20 to 1:10) mixtures as eluent to give a yellow gum of **15** (223 mg, 69% for the two steps); mp 38–40 °C; (Found: C, 79.3; H, 6.5; N, 4.7. $C_{174}H_{171}F_3IrN_9$ requires C, 79.2; H, 6.5; N, 4.8%); λ_{max} (CH_2Cl_2)/nm: 249 (log ε/dm^3 mol^{-1} cm^{-1} 4.80), 262 (4.71), 273 sh (4.61), 298 (4.29), 339 (4.12), 366 sh (3.93), 395 sh (3.61) and 433 sh (2.61); δ_H (400.2 MHz, $CDCl_3$) 0.73 (9 H, t, *J* 7.5, Pr CH_3), 1.40 and 1.50 (2 × 3 H, m, Pr CH_2), 2.07 and 2.27 (2 × 3 H, m, Pr CH_2), 2.47 and 2.64 (2 × 3 H, m, CH_2CH_2), 2.71–2.92 (54 H, m, CH_2CH_2), 5.35 (3 H, d, *J* 16.5, 1/

2NCH$_2$Ar), 5.53 (3 H, d, *J* 16.5, 1/2NCH$_2$Ar), 6.24 (3 H, d, *J* 11.4, LP H), 6.82 (6 H, m, G1-BP H), 6.88 (12 H, m, G1-BP H) and 7.04–7.28 (63 H, m, SP H & LP H); δ_F (376.6 MHz, CDCl$_3$) −115.4; *m/z* [MALDI: DCTB] Anal. Calcd for $C_{174}H_{171}F_3IrN_9$: 2634.3 (21%), 2635.3 (42%), 2636.3 (78%), 2637.3 (100%), 2638.3 (85%), 2639.3 (52%), 2640.3 (25%), 2641.3 (8%), 2642.3 (3%). Found: 2634.3 (26%), 2635.3, (51%), 2636.3 (83%), 2637.3 (100%), 2638.3 (92%), 2639.3 (56%), 2640.3 (25%), 2641.3 (11%), 2642.3 (4%) (M$^+$). Excess **14** (474 mg), which co-chromatographed with and had an identical ^{1}H NMR to an authentic sample, was also recovered.

4-[4-(2-Ethylhexyloxy)phenyl]-2-methylbut-3-yn-2-ol 17. Tetrakis(triphenylphosphine)palladium(0) (600 mg, 0.519 mmol) was added to a deoxygenated (by placing under vacuum and backfilling with argon) mixture of **16** (12.9 g, 38.8 mmol), 2-methylbut-3-yn-2-ol (4.25 g, 50.5 mmol), copper iodide (740 mg, 3.83 mmol), triethylamine (80 cm^3) and tetrahydrofuran (80 cm^3). The mixture was then deoxygenated again before being heated under argon in an oil bath held at 60 °C for 16 h. The reaction was cooled to room temperature and the solvents were removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (0:1 to 1:10) mixtures as eluent to give of **17** as a brownish oil (11.15 g, 100%); (Found: C, 79.2; H, 9.7. $C_{19}H_{28}O_2$ requires C, 79.1; H, 9.8%); λ_{max} (CH$_2$Cl$_2$)/nm: 257 (log ε/dm^3 mol^{-1} cm^{-1} 4.46), 284 sh (3.40) and 296 (3.15); ν_{max} (neat)/cm^{-1} 2229 (C≡C), 3360 (OH); δ_H (400.2 MHz, CDCl$_3$) 0.89–0.97 (6 H, m, EH CH$_3$), 1.27–1.55 (8 H, m, EH CH$_2$), 1.62 (6 H, s, CH$_3$), 1.67–1.78 (1 H, m, EH CH), 2.35 (1 H, br s, OH), 3.83 (2 H, m, ArOCH$_2$), 6.83 and 7.34 (4 H, AA′BB′, SP H); δ_C (100.6 MHz, CDCl$_3$) 11.0, 14.0, 23.0, 23.7, 29.0, 30.4, 31.5, 39.2, 65.5, 70.4, 82.0, 92.2, 114.35, 114.4, 132.9 and 159.3; *m/z* [TOF ES$^+$] 271.2 (M-OH), 289.2 (MH$^+$).

1-(2-Ethylhexyloxy)-4-acetylenylbenzene 18. A mixture of **17** (38.8 g, 134 mmol), heptane (650 cm^3) and sodium *tert*-butoxide (3.75 g, 39.0 mmol) was heated under argon in an oil bath held at 100 °C for 17 h. The mixture was allowed to cool to room temperature and the solvent was removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (1:80 to 1:5) mixtures as eluent to give **18** as a brownish oil (28.9 g, 94%); (Found: C, 83.6; H, 9.6. $C_{16}H_{22}O$ requires C, 83.4; H, 9.6%); λ_{max} (CH$_2$Cl$_2$)/nm: 255 (log ε/dm^3 mol^{-1} cm^{-1} 4.33), 283 (3.42), 294 (3.24), 302 sh (2.95), 322 (2.99), and 345 (2.90);ν_{max} (neat)/cm^{-1} 2108 (C≡C); δ_H (400.2 MHz, CDCl$_3$) 0.88–0.99 (6 H, m, EH CH$_3$), 1.29–1.59 (8 H, m, EH CH$_2$), 1.69–1.80 (1 H, m, EH CH), 3.02 (1 H, s, C≡CH), 3.86 (2 H, m, ArOCH$_2$), 6.86 and 7.45 (4 H, AA′BB′, SP H); δ_C (100.6 MHz, CDCl$_3$) 11.0, 14.0, 23.0, 23.8, 29.0, 30.4, 39.3, 70.5, 75.6, 83.8, 113.8, 114.4, 133.5 and 159.7; *m/z* [TOF CI$^+$] 231.2 (MH$^+$).

3,5-Bis[2-(4-{2-ethylhexyloxy}phenyl)acetylen-1-yl]benzaldehyde 19. Tetrakis(triphenylphosphine)palladium(0) (1.42 g, 1.23 mmol) was added to a deoxygenated (by placing under vacuum and backfilling with argon four times) mixture of 3,5-dibromobenzaldehyde (7.58 g, 28.7 mmol), **18** (18.0 g, 78.1 mmol), copper iodide (740 mg, 3.89 mmol), triethylamine (76 cm^3), and tetrahydrofuran (76 cm^3). The mixture was deoxygenated again and then heated under argon in an oil bath held at 72 °C for 61 h. The reaction was cooled to room temperature and the solvents were removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (0:1 to 1:5) mixtures as eluent to give **19** as a brownish oil (14.3 g, 88%); (Found: C, 83.1; H, 8.2. $C_{39}H_{46}O_3$ requires C, 83.2; H, 8.2%); λ_{max} (CH$_2$Cl$_2$)/nm: 256 (log ε/dm^3 mol^{-1} cm^{-1} 4.60), 302 (4.75), 315 (4.75) and 359 sh (3.75);ν_{max} (neat)/cm^{-1} 1704 (C═O), 2211 (C≡C); δ_H (400.1 MHz, CDCl$_3$) 0.90–0.98 (12 H, m, EH CH$_3$), 1.30–1.55 (16 H, m, EH CH$_2$), 1.70–1.80 (2 H, m, EH CH), 3.88 (4 H, m, ArOCH$_2$), 6.90 & 7.48 (8 H, AA′BB′, SP H), 7.88 (1 H, dd, *J* 1.5, *J* 1.5, G1-BP H), 7.92 (2 H, d, *J* 1.5, G1-BP H) and 10.0 (1 H, s, ArCHO); δ_C (100.6 MHz, CDCl$_3$) 11.1, 14.1, 23.0, 23.8, 29.0, 30.4, 39.2, 70.5, 86.0, 91.7, 114.1, 114.6, 125.15, 131.3, 133.2, 136.5, 139.1, 159.9 and 191.0; *m/z* [microTOF ES$^+$] 585.3 (M$^+$ + Na).

1-[3,5-Bis(2-{4-[2-ethylhexyloxy]phenyl}acetylen-1-yl)phenyl]-2,2-dibromovinylene 20. Triphenylphosphine (4.11 g, 15.6 mmol) was added to a mixture of **19** (2.20 g, 3.91 mmol), carbon tetrabromide (2.60 g, 7.84 mmol), and dichloromethane (22 cm^3) (Note: the reaction is exothermic). The mixture was stirred at room temperature under argon for 4 h and then passed through a plug of silica using dichloromethane as the eluent. The filtrate was collected and the solvent removed. The residue was purified by column chromatography over silica using dichloromethane:-light petroleum (0:1 to 1:10) mixtures as eluent to give **20** as a brownish oil (2.64 g, 94%); (Found: C, 66.9; H, 6.5. $C_{40}H_{46}Br_2O_2$ requires C, 66.9; H, 6.45%); λ_{max} (CH$_2$Cl$_2$)/nm: 259 sh (log ε/dm^3 mol^{-1} cm^{-1} 4.61), 269 (4.64), 301 (4.83), and 317 (4.80); ν_{max} (neat)/cm^{-1} 2211 (C≡C); δ_H (400.2 MHz, CDCl$_3$) 0.93–1.01 (12 H, m, EH CH$_3$), 1.31–1.61 (16 H, m, EH CH$_2$), 1.71–1.81 (2 H, m, EH CH), 3.88 (4 H, m, ArOCH$_2$), 6.91 and 7.50 (8 H, AA′BB′, SP H), 7.44 (1 H, s, Br$_2$C═CH), 7.61 (2 H, m, G1-BP H) and 7.66 (1 H, dd, *J* 1.5, *J* 1.5, G1-BP H); δ_C (100.6 MHz, CDCl$_3$) 11.1, 14.1, 23.0, 23.8, 29.0, 30.4, 39.2, 70.5, 86.7, 90.7, 91.3, 114.47, 114.53, 124.3, 130.3, 133.1, 133.9, 135.5, 135.6 and 159.6; *m/z* [microTOF ES$^+$] 739.2, 741.2, 743.2 (M$^+$ + Na).

1-[3,5-Bis(2-{4-[2-ethylhexyloxy]phenyl}acetylen-1-yl)phenyl]-2-bromoacetylene 21. A mixture of **20** (1.52 g, 2.12 mmol), sodium *tert*-butoxide (406 mg, 4.23 mmol), and toluene (30 cm^3) was heated under argon in an oil bath held at 50 °C for 15 h. The mixture was allowed to cool to room temperature and the solvent was removed. Water (10 cm^3) was added to the residue. The mixture was extracted with dichloromethane (3 × 15 cm^3). The dichloromethane extracts were combined, washed with brine (20 cm^3), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (0:1 to 1:10) mixtures as eluent to afford **21** as a pale yellow oil (1.24 g, 92%); (Found: C, 75.4; H, 7.0. $C_{40}H_{45}BrO_2$ requires C, 75.3; H, 7.1%); λ_{max} (CH$_2$Cl$_2$)/nm: 254 sh (log ε/dm^3 mol^{-1} cm^{-1} 4.53), 266 (4.56), 306 (4.76) and 318 (4.75);ν_{max} (neat)/cm^{-1} 2211 (C≡C); δ_H (400.1 MHz, CDCl$_3$) 0.88–1.00 (12 H, m, EH CH$_3$), 1.28–1.61 (16 H, m, EH CH$_2$), 1.70–1.82 (2 H, m, EH CH), 3.87 (4 H, m, ArOCH$_2$), 6.89 & 7.45 (8 H, AA′BB′, SP H), 7.51 (2 H, d, *J* 1.5, G1-BP H) and 7.62 (1 H, dd, *J* 1.5, *J* 1.5, G1-BP H); *m/z* [microTOF ES$^+$] 636.3, 638.3 (M$^+$).

[3,5-Bis(2-{4-[2-ethylhexyloxy]phenyl}acetylen-1-yl)phenyl]acetylene 22. A solution of **21** (220 mg, 0.345 mmol) in ether (10 cm^3) was cooled to −78 °C under argon. *Tert*-butyllithium (0.32 cm^3, 0.552 mmol) was added carefully to the reaction. The mixture was stirred at −78 °C for 2.5 h and then water (1 cm^3) *was added very carefully dropwise to the reaction mixture while at−78 °C*. After 30 min, the mixture was warmed to room temperature and diluted with water (5 cm^3) and ether (6 cm^3). The organic layer was separated and the aqueous layer was extracted with ether (3 × 10 cm^3). The organic layers were combined, washed with brine (12 cm^3), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent was removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (0:1 to 1:5) mixtures as eluent to give **22** as a pale yellow oil (180 mg, 93%); (Found: C, 86.05; H, 8.4. $C_{40}H_{46}O_2$ requires C, 86.0; H, 8.3%); λ_{max} (CH_2Cl_2)/nm: 244 sh (log ε/dm^3 mol^{-1} cm^{-1} 4.65), 254 (4.69), 263 sh (4.66), 303 (4.94) and 317 (4.93); ν_{max} (neat)/cm^{-1} 2209 (C≡C), 3297 (C≡C–H); δ_H (400.1 MHz, $CDCl_3$) 0.85–0.99 (12 H, m, EH CH_3), 1.27–1.60 (16 H, m, EH CH_2), 1.69–1.80 (2 H, m, EH CH), 3.10 (C≡C–H), 3.87 (4 H, m, ArOCH_2), 6.89 & 7.46 (8 H, AA′BB′, SP H), 7.56 (2 H, m, G1-BP H) and 7.63 (1 H, m, G1-BP H); δ_C (100.6 MHz, $CDCl_3$) 11.1, 14.1, 23.0, 23.8, 29.0, 30.4, 39.3, 70.5, 78.1, 82.2, 86.4, 90.8, 114.4, 114.5, 122.7, 124.3, 133.1, 133.9, 134.3 and 159.7; *m*/*z* [microTOF ES+] 581.3 (M^+ + Na).

Methyl-4-fluoro-3-iodobenzoate. A solution of 3-iodo-4-fluorotoluene (5.00 g, 21.2 mmol), water (33 cm^3), and pyridine (10 cm^3) was heated in an oil bath held at 60 °C. Potassium permanganate (10.4 g, 65.8 mmol) was added in portions to the hot mixture over a 5 h period. After addition, the reaction mixture was stirred for another 2.5 h and then room temperature for 12 h. The reaction was filtered and the manganese dioxide was washed with water (3 × 7 cm^3). The filtrate was collected and the solution concentrated. Hydrochloric acid (3 M, 40 cm^3) was added to the residue, and the mixture was extracted with ether (4 × 20 cm^3). The ether extracts were combined, washed with brine (30 cm^3), and dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent was removed to give crude *3-iodo-4-fluorobenzoic acid* (≈2.52 g, ≈45%) as a white solid, which was used without further purification. Concentrated sulfuric acid (30 drops) was carefully added to a solution of the crude 4-fluoro-3-iodobenzoic acid (≈2.52 g) in methanol (30 cm^3). The mixture was heated at reflux under argon for 18 h and then allowed to cool to room temperature. The solvent was removed and the residue was purified by column chromatography over silica using dichloromethane:light petroleum (1:20 to 1:3) mixtures as eluent to give *methyl-4-fluoro-3-iodobenzoate* as a colourless oil (2.59 g, 97%), which solidified to a white solid at room temperature on standing; mp 42–43 °C; (Found: C, 34.4; H, 2.1. $C_8H_6FIO_2$ requires C, 34.3; H, 2.2%); λ_{max} (CH_2Cl_2)/nm: 278 sh (log ε/dm^3 mol^{-1} cm^{-1} 2.93) and 289 sh (2.77); ν_{max} (film)/cm^{-1} 1723 (C═O); δ_H (400.2 MHz, $CDCl_3$) 3.93 (3 H, s, CH_3), 7.12 (1 H, m, ArH), 8.02 (1 H, m, ArH) and 8.47 (1 H, m, ArH); δ_F (376.5 MHz, $CDCl_3$) −86.7.

Methyl-3-[2-(3,5-bis{2-[4-(2-ethylhexyloxy)phenyl]acetylen-1-yl}-phenyl)acetylen-1-yl]-4-fluorobenzoate 28. Tetrakis(triphenylphosphine)palladium(0) (103 mg, 0.09 mmol) was added to a deoxygenated (by placing under vacuum and backfilling with argon) mixture of methyl-4-fluoro-3-iodobenzoate (250 mg, 0.89 mmol), **22** (700 mg, 1.25 mmol), copper iodide (34 mg, 0.19 mmol), triethylamine (5 cm^3), and tetrahydrofuran (5 cm^3). The mixture was deoxygenated again and then heated under argon in an oil bath held at 77 °C for 14 h. The mixture was cooled to room temperature and the solvents were removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (1:40 to 1:3) mixtures as eluent to give **28** as a colourless oil (635 mg, 100%); (Found: C, 81.1; H, 7.3. $C_{48}H_{51}FO_4$ requires C, 81.1; H, 7.2%); λ_{max} (CH_2Cl_2)/nm: 259 sh (log ε/dm^3 mol^{-1} cm^{-1} 4.68), 273 sh (4.74), 290 sh (4.95), 301 sh (5.03), 308 (5.07) and 319 sh (4.92); ν_{max} (neat)/cm^{-1} 1728 (C═O), 2211 (C≡C); δ_H (400.2 MHz, $CDCl_3$) 0.89–0.99 (12 H, m, EH CH_3), 1.28–1.58 (16 H, m, EH CH_2), 1.69–1.80 (2 H, m, EH CH), 3.87 (4 H, m, ArOCH_2), 3.94 (3 H, s, $COOCH_3$), 6.90 and 7.48 (8 H, AA′BB′, SP H), 7.18 (1 H, t, *J* 8.5, LP H), 7.48 (4 H, 1/2AA′BB′, SP H), 7.64 (3 H, m, G1-BP H), 8.04 (1 H, m, LP H) and 8.24 (1 H, dd, *J* 2, *J* 7, LP H); δ_F (376.6 MHz, $CDCl_3$) −102.7; *m*/*z* [TOF ES+] 711.3 (MH^+).

Methyl-3-[2-(3,5-bis{2-[4-(2-ethylhexyloxy)phenyl]ethylen-1-yl}-phenyl)ethylen-1-yl]-4-fluorobenzoate 29. A solution of **28** (635 mg, 0.89 mmol), ethyl acetate (10 cm^3), and methanol (10 cm^3) was deoxygenated (by placing under vacuum and backfilling with argon) four times. 10% Palladium on carbon (130 mg) was added to the mixture, which was then deoxygenated further four times. A balloon filled with hydrogen was attached and the reaction mixture was briefly degassed and backfilled with hydrogen four times. The reaction was stirred at room temperature under hydrogen for 14 h. The mixture was passed through a plug of silica using dichloromethane as eluent (60 cm^3) (the silica was poured into excess water immeditely to quench the catalyst). The filtrate was collected and the solvent removed. The mixture was purified by column chromatography over silica using dichloromethane:light petroleum (1:30 to 1:3) mixtures as eluent to give **29** as a colourless oil (612 mg, 95%); (Found: C, 79.8; H, 8.8. $C_{48}H_{63}FO_4$ requires C, 79.7; H, 8.8%); λ_{max} (CH_2Cl_2)/nm: 279 (log ε/dm^3 mol^{-1} cm^{-1} 3.67) and 286 (3.55);ν_{max} (neat)/cm^{-1} 1726 (C═O); δ_H (400.1 MHz, $CDCl_3$) 0.87–0.96 (12 H, m, EH CH_3), 1.26–1.55 (16 H, m, EH CH_2), 1.65–1.76 (2 H, m, EH CH), 2.76–2.97 (12 H, m, CH_2CH_2), 3.82 (4 H, m, ArOCH_2), 3.90 (3 H, s, $COOCH_3$), 6.80–6.87 (7 H, m, SP H & G1-BP H), 7.05–7.11 (5 H, m, SP H & LP H) and 7.88–7.94 (2 H, m, LP H); δ_F (376.6 MHz, $CDCl_3$) −111.4; *m*/*z* [TOF ES+] 723.3 (MH^+).

Methyl-3,5-bis[2-(4-{2-ethylhexyloxy}phenyl)acetylen-1-yl]benzoate 23. Tetrakis(triphenylphosphine)palladium(0) (85 mg, 0.074 mmol) was added to a deoxygenated (by placing under vacuum and backfilling with argon) mixture of methyl-3,5-diiodobenzoate (410 mg, 1.06 mmol), **18** (730 mg, 3.17 mmol), copper iodide (60 mg, 0.315 mmol), triethylamine (6 cm^3), and tetrahydrofuran (6 cm^3). The mixture was deoxygenated again and then heated under argon in an oil bath held at 77 °C for 28 h. The reaction was cooled to room temperature and the solvents were removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (1:40 to 1:3) mixtures as eluent to give **23** as a light yellow oil (610 mg, 97%); (Found: C, 81.1; H, 8.0. $C_{40}H_{48}O_4$ requires C, 81.0; H, 8.2%); λ_{max} (CH_2Cl_2)/nm: 247 sh (log ε/dm^3 mol^{-1} cm^{-1} 4.67), 259 (4.72), 305 (4.98) and 314 sh (4.97); ν_{max} (neat)/cm^{-1} 1728 (C=O), 2212 (C≡C); δ_H (400.1 MHz, $CDCl_3$) 0.87–0.98 (12 H, m, EH CH_3), 1.29–1.59 (16 H, m, EH CH_2), 1.69–1.80 (2 H, m, EH CH), 3.88 (4 H, m, $ArOCH_2$), 3.95 (3 H, s, $COOCH_3$), 6.90 and 7.47 (8 H, AA′BB′, SP H), 7.82 (1 H, dd, *J* 1.5, *J* 1.5, G1-BP H) and 8.10 (2 H, m, G1-BP H); δ_C (100.6 MHz, $CDCl_3$) 11.1, 14.1, 23.0, 23.8, 29.0, 30.5, 39.3, 52.4, 70.6, 86.4, 91.0, 114.4, 114.6, 124.5, 130.6, 131.5, 133.1, 137.8, 159.8 and 165.9; *m*/*z* [TOF ES$^+$] 593.3 (M$^+$).

Methyl-3,5-bis[2-(4-{2-ethylhexyloxy}phenyl)ethylen-1-yl]benzoate 24. 10% Palladium on carbon (125 mg) was added to a solution of **23** (600 mg, 1.01 mmol), ethyl acetate (20 cm^3), and methanol (20 cm^3). The mixture was deoxygenated (by placing under vacuum and backfilling with argon) four times. A hydrogen balloon was attached and the mixture was briefly degassed under vacuum and backfilled with hydrogen four times. The mixture was stirred at room temperature under hydrogen for 14 h and then passed through a plug of silica using dichloromethane as eluent (the silica was poured into excess water immediately to quench the catalyst). The filtrate was collected and the solvent was removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (1:40 to 1:3) mixtures as eluent to give **24** as a colourless oil (587 mg, 97%); (Found: C, 80.0; H, 9.45. $C_{40}H_{56}O_4$ requires C, 80.0; H, 9.4%); λ_{max} (CH_2Cl_2)/nm: 280 (log ε/dm^3 mol^{-1} cm^{-1} 3.83), 286 (3.81) and 295 sh (3.37); ν_{max} (neat)/cm^{-1} 1726 (C=O); δ_H (400.1 MHz, $CDCl_3$) 0.86–0.97 (12 H, m, EH CH_3), 1.27–1.60 (16 H, m, EH CH_2), 1.67–1.76 (2 H, m, EH CH), 2.79–2.93 (8 H, m, CH_2CH_2), 3.82 (4 H, m, $ArOCH_2$), 3.92 (3 H, s, $COOCH_3$), 6.83 & 7.07 (8 H, AA′BB′, SP H), 7.10 (1 H, s, G1-BP H) and 7.73 (2 H, s, G1-BP H); δ_C (100.6 MHz, $CDCl_3$) 11.1, 14.1, 23.0, 23.8, 29.0, 30.5, 37.0, 38.0, 39.4, 52.0, 70.5, 114.4, 127.2, 129.2, 130.1, 133.2, 133.6, 142.1, 157.7 and 167.4; *m*/*z* [TOF ES$^+$] 601.4 (MH$^+$).

3,5-Bis[2-(4-{2-ethylhexyloxy}phenyl)ethylen-1-yl]benzyl bromide 26. Lithium aluminium hydride (72 mg, 1.90 mmol) was added to a mixture of **24** (570 mg, 0.95 mmol) and anhydrous tetrahydrofuran (20 cm^3). The reaction mixture was stirred at room temperature under argon for 40 min and then heated in an oil bath held at 60 °C for 2 h. The mixture was allowed to cool to room temperature and carefully poured into a mixture of ice and water (≈60 cm^3). The mixture was extracted with ethyl acetate (6 × 20 cm^3). The ethyl acetate extracts were combined, washed with brine (50 cm^3), dried over anhydrous magnesium sulfate and filtered. The filtrate was collected and the solvent was removed to give crude *methyl-3,5-bis[2-(4-{2-ethylhexyloxy}phenyl)ethylen-1-yl]benzyl alcohol* **25** (≈543 mg) as a colourless oil, which was used directly in the next step. Phosphorus tribromide (0.4 cm^3, 4.21 mmol) was added to **25** (≈543 mg, 0.95 mmol) and then the mixture was heated under argon in an oil bath held at 90 °C for 14 h. The mixture was cooled to room temperature and diluted with ether (8 cm^3). The mixture was cooled to 0–2 °C and slowly and carefully quenched with water (4 cm^3). The two layers were separated and the aqueous layer was extracted with ether (3 × 3 cm^3). The organic layers were combined, washed with brine (8 cm^3), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent was removed. The residue was purified by column chromatography over silica using dichloromethane:light petroleum (1:30 to 1:5) mixtures as eluent to give **26** as a colourless oil (560 mg, 93% for the two steps with respect to **24**); (Found: C, 73.8; H, 8.6. $C_{39}H_{55}BrO_2$ requires C, 73.7; H, 8.7%); λ_{max} (CH_2Cl_2)/nm: 279 (log ε/dm^3 mol^{-1} cm^{-1} 3.76) and 286 (3.68); δ_H (400.2 MHz, $CDCl_3$) 0.93–1.04 (12 H, m, EH CH_3), 1.33–1.64 (16 H, m, EH CH_2), 1.72–1.83 (2 H, m, EH CH), 2.90 (8 H, s, CH_2CH_2), 3.88 (4 H, m, $ArOCH_2$), 4.50 (2 H, s, $ArCH_2Br$), 6.90 and 7.13 (8 H, A′BB′, SP H), 6.96 (1 H, br dd, G1-BP H) and 7.09 (2 H, br d, G1-BP H); δ_C (100.6 MHz, $CDCl_3$) 11.1, 14.1, 23.0, 23.8, 29.0, 30.5, 33.9, 36.9, 38.0, 39.4, 70.4, 114.4, 126.8, 129.0, 129.2, 133.3, 137.6, 142.4 and 157.7; *m*/*z* [microTOF ES$^+$] 657.3, 659.3 (M$^+$ + Na).

1-[3,5-Bis(2-{4-[2-ethylhexyloxy]phenyl}ethylen-1-yl)benzyl]-5-[4-fluoro-3-(2-{3,5-bis[2-(4-{2-ethylhexyloxy}phenyl)ethylen-1-yl]-phenyl}ethylen-1-yl)phenyl]-3-*n*-propyl-1*H*-1,2,4-triazole 33. A mixture of **29** (2.49 g, 3.45 mmol), lithium hydroxide (165 mg, 6.89 mmol), water (9 cm^3), methanol (9 cm^3), and tetrahydrofuran (20 cm^3) was heated under argon in an oil bath held at 63 °C for 4 h. The reaction mixture was allowed to cool to room temperature and the solvent was removed. Hydrochloric acid (3 M, 20 cm^3) was added to the residue. The mixture was extracted with dichloromethane (3 × 30 cm^3). The dichloromethane extracts were combined, washed with brine (35 cm^3), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent was removed. The mixture was purified by column chromatography over silica using dichloromethane:-light petroleum (0:1 to 1:0) and ethyl acetate:dichloromethane (1:4 to 2:1) mixtures as eluent to give *3-[2-(3,5-bis{2-[4-(2-ethylhexyloxy)phenyl]ethylen-1-yl}phenyl)ethylen-1-yl]-4-fluorobenzoic acid* **30** (2.19 g, 90%) as a colourless oil, which was used immediately. A mixture of thionyl chloride (1.1 cm^3) and **30** (2.17 g, 3.06 mmol) was heated at reflux for 13 h under argon. The reaction was allowed to cool and the excess thionyl chloride was removed by evaporation under reduced pressure to give crude *3-[2-(3,5-bis{2-[4-(2-ethylhexyloxy)phenyl]ethylen-1-yl}phenyl)-ethylen-1-yl]-4-fluorobenzoyl chloride* **31** (≈2.23 g, ≈3.06 mmol) as a brownish oil, which was used without purification. A solution of triethylamine (1.2 cm^3) in chloroform (6 cm^3) was added dropwise to a mixture of **31** (≈2.23 g, ≈3.06 mmol), ethyl butyrimidate hydrochloride (510 mg, 3.34 mmol), and chloroform (10 cm^3) under argon. The reaction was stirred at room temperature for 67 h. The solvent was removed and the residue was dissolved into a mixture of water (30 cm^3) and dichloromethane (30 cm^3). The aqueous layer was separated and the organic layer was washed with water (4 × 20 cm^3) and brine (20 cm^3), dried over anhydrous sodium sulfate, and filtered. The filtrate was collected and the solvent was removed to give **32** (≈2.45 g) as a brownish oil, which was used without further purification. **26** (900 mg, 1.42 mmol) was added in small portions to a mixture of hydrazine monohydrate (369 mg, 7.36 mmol) and ethanol (10 cm^3) heated at reflux under air. After addition (2 h), the mixture was kept at reflux under argon for 26 h. The reaction was allowed to cool to room temperature and the solvent was removed. The residue was dissolved in dichloromethane (40 cm^3), dried over anhydrous sodium sulfate, and filtered. The filtrate was collected and the solvent was removed under vacuum to give a colourless oil of *3,5-bis[2-(4-{2-ethylhexyloxy}phenyl)ethylen-1-yl]benzyl hydrazine* **27** ($\approx$830 mg), which was used without further purification. A solution of **27** in chloroform (5 cm^3) was added to a solution of **32** (1.00 g, 1.24 mmol) in chloroform (8 cm^3) under argon. The reaction was stirred at room temperature for 14 h. The solvent was removed and the residue was purified by column chromatography over silica using ethyl acetate:light petroleum (1:50 to 1:10) mixtures as eluent to give **33** as a colourless oil (929 mg, 49% for the two steps with respect to **26**); (Found: C, 81.4; H, 9.3; N, 3.1. $C_{90}H_{122}FN_3O_4$ requires C, 81.3; H, 9.25; N, 3.2%); λ_{max} (CH_2Cl_2)/nm: 272 sh (log ε/dm^3 mol^{-1} cm^{-1} 3.96), 277 (3.98) and 286 (3.87); δ_H (400.2 MHz, $CDCl_3$) 0.87–1.02 (24 H, m, EH CH_3), 1.09 (3 H, t, *J* 7.4, Pr CH_3), 1.30–1.62 (32 H, m, EH CH_2), 1.70–1.81 (4 H, m, EH CH), 1.92 (2 H, m, Pr CH_2), 2.83 (20 H, br s, CH_2CH_2), 2.95 (2 H, m, Pr CH_2), 3.85 (8 H, m, $ArOCH_2$), 5.27 (2 H, s, NCH_2Ar), 6.78–6.91 (13 H, m, SP H & G1-BP H), 6.93 (1 H, br s, G1-BP H), 7.01–7.16 (9 H, m, SP H & LP H), 7.38 (1 H, br m, LP H) and 7.49 (1 H, br dd, LP H); δ_F (376.6 MHz, $CDCl_3$) −115.6; *m*/*z* [MALDI: DCTB] Anal. Calcd for $C_{90}H_{122}FN_3O_4$: 1327.9 (98%), 1328.9 (100%), 1329.9 (50%), 1331.0 (17%), 1332.0 (3%). Found: 1328.0 (83%), 1329.0 (100%), 1330.0 (67%), 1331.0 (36%), 1332.0 (3%) (M^+).

Tris-*fac*-[1-(3,5-Bis{2-[4-(2-ethylhexyloxy)phenyl]ethylen-1-yl}-benzyl)-5-(4-fluoro-3-{2-[3,5-bis(2-{4-[2-ethylhexyloxy]phenyl}-ethylen-1-yl)phenyl]ethylen-1-yl}phenyl)-3-*n*-propyl-1*H*-1,2,4-triazolyl]iridium(III) 34. A mixture of **33** (355 mg, 0.27 mmol), iridium(III) chloride trihydrate (40 mg, 0.11 mmol), water (0.5 cm^3), and 2-(*n*-butoxy)ethanol (1.5 cm^3) was heated at reflux under argon for 14.5 h. The mixture was allowed to cool to room temperature. Water (10 cm^3) was added to the mixture and the liquid was removed. This was repeated twice. The residue was dissolved in dichloromethane (20 cm^3) and dried over anhydrous sodium sulfate, and filtered. The filtrate was collected and the solvent was removed to give a yellow–orange oil ($\approx$400 mg) as a mixture of the iridium chloro-bridged dimer and **33**. A mixture of the dimer/ligand mixture, **33** (600 mg, 0.45 mmol), and silver trifluoromethanesulfonate (58 mg, 0.23 mmol) was heated in an oil bath held at 166 °C for 18 h. The reaction was allowed to cool to room temperature and the mixture was purified by column chromatography over silica using dichloromethane:light petroleum (1:60 to 1:2) and then ethyl acetate:dichloromethane (1:5) mixtures as eluent. The main band was collected and further purified with a chromatotron using dichloromethane:light petroleum (1:10 to 1:2) mixtures as eluent to give **34** as a pale yellow oil (220 mg, 47% for the two steps); (Found: C, 77.7; H, 8.8; N, 3.1. $C_{270}H_{363}F_3IrN_9O_{12}$ requires C, 77.65; H, 8.8; N, 3.0%); λ_{max} (CH_2Cl_2)/nm: 250 sh (log ε/dm^3 mol^{-1} cm^{-1} 4.88), 264 (4.81), 275 (4.83), 286 sh (4.60), 297 sh (4.37), 339 (4.19), 367 sh (3.95), 395 sh (3.66) and 433 sh (2.76); δ_H (400.2 MHz, $CDCl_3$) 0.69 (9 H, t, *J* 7.5, Pr CH_3), 0.87–0.95 (72 H, m, EH CH_3), 1.26–1.56 (102 H, m, EH CH_2 & Pr CH_2), 1.64–1.77 (12 H, m, EH CH), 2.03 & 2.20 (2 × 3 H, m, Pr CH_2), 2.52–2.85 (60 H, m, CH_2CH_2), 3.80 (24 H, m, $ArOCH_2$), 5.41 (3 H, d, *J* 16.5, 1/2NCH_2Ar), 5.53 (3 H, d, *J* 16.5, 1/2NCH_2Ar), 6.22 (3 H, *J* 11.5, LP H), 6.74–6.84 (36 H, m, SP H & G1-BP H), 6.87 (6 H, s, G1-BP H), 6.96 (12 H, 1/2AA′BB′, SP H), 7.03 (12 H, 1/2AA′BB′, SP H) and 7.15 (3 H, d, *J* 7.5, LP H); δ_F (376.6 MHz, $CDCl_3$) −115.6; *m*/*z* [MALDI: DCTB] Anal. Calcd for $C_{270}H_{363}F_3IrN_9O_{12}$: 4171.8 (8%), 4172.8, (26%), 4173.8 (55%), 4174.8 (85%), 4175.8 (100%), 4176.8 (92%), 4177.8 (64%), 4178.8 (36%), 4179.8 (17%), 4180.8 (7%), 4181.8 (3%). Found: 4171.9 (17%), 4172.9, (36%), 4173.9 (60%), 4174.9 (79%), 4175.8 (100%), 4176.9 (68%), 4177.9 (46%), 4178.9 (34%), 4179.9 (14%), 4180.9 (9%), 4181.9 (4%) (M^+). Excess **33** (533 mg), which co-chromatographed with and had an identical ^{1}H NMR to an authentic sample, was also recovered.

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