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A convergent route to poly(phenyl ketone ether) dendrons

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Abstract—A series of poly(phenyl ketone) dendrons have been constructed using a convergent strategy. An aryl fluoro-substituent is deactivated towards nucleophilic substitution by protection of a para-ketone as an acetal. This allows coupling to an activated aryl fluoride. Subsequent deprotection of the acetyl group then activates the first fluoro-substituent and allows the next generation of the dendron to be added. The synthesis of higher generations is complicated by a scrambling reaction, which lowers the yields.

1. Introduction

Ever since their realisation in the 1980s,[1] dendrimers have been widely studied due to their unique properties.[2] The exterior or interior can be decorated with functional groups for applications such as encapsulation,[3] light harvesting,[4] catalysis[5] or electroluminescence.[6] Most dendrimers are constructed using flexible linkers, as their chemistry and processing tend to be easier. However, in certain applications where structural integrity is important, rigid branches may prove important. Examples of rigid dendrimers include those based on branched phenylenes[7] and phenylacetylenes.[8] While dendrimers have been the focus of research in the past, more recently dendrons have proved their importance in their own right as solubilising and rigidifying modifiers for polymers.[9]

There are two distinct routes for dendrimer/dendron synthesis, namely the divergent or convergent step-wise growth methods. The divergent method of dendrimer synthesis involves the build up of successive layers of protected, polyfunctional monomers starting from a central core. Several addition/activating steps are carried out until the desired dendrimer size is obtained. An increasing number of chain end monomers at the periphery is produced as the dendrimer is built up. An example of this is the synthesis of poly(amidoamine) PAMAM Starburst dendrimers,[1c,d] where ammonia acts as the core molecule. As successive generations are built up it gets increasingly difficult to obtain high yielding reactions and the maximum size of the dendrimer is limited due to the level of steric crowding at the surface. Another problem is in the purification at each generation, as any single defect in the dendrimer makes only a small difference to its properties.

The convergent method on the other hand differs in the fact that the synthesis starts from the periphery monomer units and works inwards to form dendrons or 'wedges'. These wedges (once the desired size is obtained) can be attached to a polyfunctional core to form the dendrimer. The convergent method has the advantage in the fact that in each step there are only two reactions (i.e., two monomers/dendrons in the *n*th generation couple to the appropriate functionality of the monomer unit in the $(n-1)$th generation) and the number of reaction sites does not increase with increasing size of the dendrimer, unlike in the divergent approach. However, if the dendrons become too big, reactivity may become impaired due to the large amount of crowding that develops near the focal point.

We were interested in the possible use of dendrimers and dendrons as high glass transition temperature (T_g) cross-linkers and polymer modifiers. For these purposes, the exterior needed to be decorated with (protected) phenolic groups, and the branching linkers needed to be thermally and oxidatively stable. The high T_g was hoped to be afforded by the use of rigid branching units. While the T_g of un-cross-linked dendrimers seems to be determined by the outer surface functionality as much by the nature of the branching linkages,[10] no studies have been made on cross-linked materials. The diaryl ketone linkage was chosen as being suitable as the T_g of linear poly(phenyl ketones) ranges from 150 to 220 °C.[11] There are two main routes known for the synthesis of polyphenyl ketone dendrimers. The first was a convergent route, which used an oxidative step to activate the fluorophenyl group towards further nucleophilic substitution (Scheme 1a).[12] This was ruled out in the present case for two reasons. The branching units in our case were ethers, which may activate the phenyl unit towards oxidation. As

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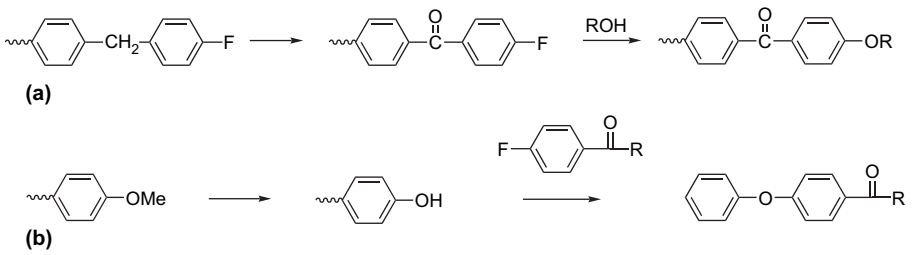


Scheme 1.

well, the oxidation may prove less selective or lower yielding as the size of the dendrimer increases. The second divergent method used the deprotection of methoxy phenyl ethers with BBr_3 or $AlCl_3$ to expose new phenoxy-groups (Scheme 1b).[13]

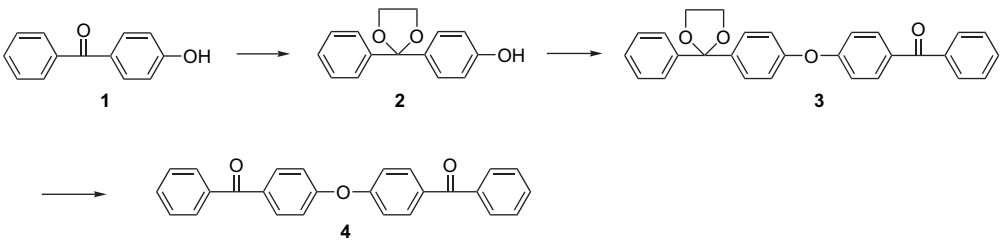
Dendrimers normally use a protection–deprotection scheme in order to selectively couple units together. The most obvious protection chemistry for the aromatic ketones would appear to be the use of cyclic acetals, which can be cleanly deprotected under mildly acidic conditions. Cyclic acetals have been used to protect fluorophenyl ketones in the synthesis of pharmaceutical derivatives, though in these instances the acetal groups were used to protect the ketone than to control the activation of the fluoro-substituent as here.[14] They have also been used to functionalise the carbonyl groups of poly(phenyl ketones) to give improved solubility over the parent polymer.[15] In that particular case, though, the acetal groups were added after the nucleophilic polymerisation step.

2. Results

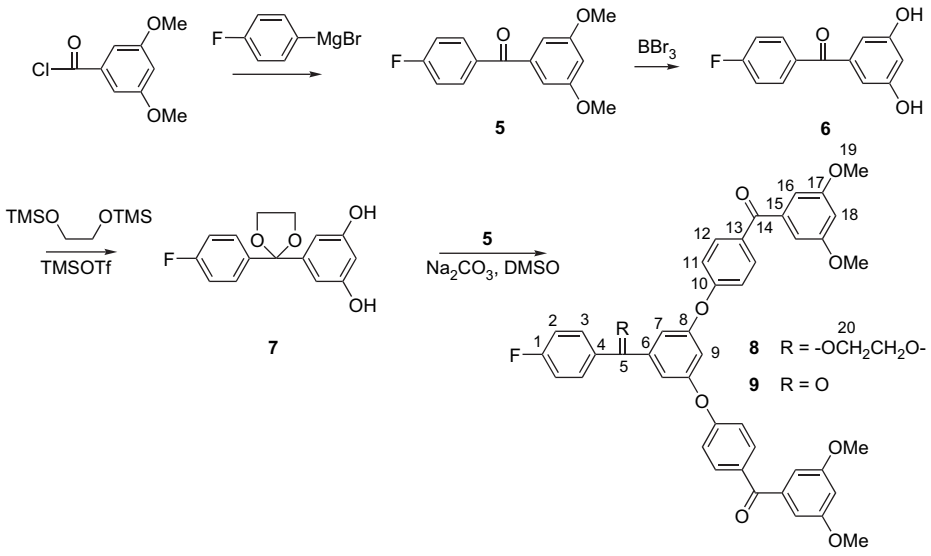
We were unsure whether a simple acetal could withstand the high temperatures and polar solvents usually used in aromatic nucleophilic substitutions. To this end, some model chemistry was undertaken in order to prove the concept. Formation of an acetal of 4-hydroxyphenyl ketone **1** was attempted under standard conditions (ethylene glycol, acid, azeotropic removal of water), but even after 5 days, only starting material could be recovered. It was possibly due to that the phenolic group was interfering in the reaction. Diaryl ketones appear difficult to protect with acetal groups at the best of times and prolonged reaction times (5 days or more) have often been employed.[15] A milder literature procedure to protect aromatic ketones involving 1,2-bis(trimethylsiloxy)ethane was then tried.[16] This reaction, which requires the use of a catalyst, trimethylsilyl trifluoromethanesulfonate, went in reasonable yield (71%) after only 3 h, the remainder being the starting material (Scheme 2). The unprotected phenolic group did not appear to interfere in the reaction. The protected ketone **2** was then reacted with 4-fluorophenyl phenyl ketone **3** using sodium carbonate as base at 160 °C to give **6** in 81% isolated yield without any apparent side products (Scheme 2). The reaction appeared clean, with no other products isolated. Gratifyingly, the cyclic acetal showed no signs of instability at those temperatures and conditions. Deprotection was cleanly performed by heating in acetone in the presence of an acid catalyst to give diketone **4** in 93% yield from **3**. Our work would seem to be the first to directly protect an activated arylfluorine group via the use of acetal protection chemistry.

The key dihydroxyketone **6** was prepared in two steps from the reaction of 4-fluorophenyl magnesium chloride with 3,5-dimethoxybenzoyl chloride to give **5**, followed by deprotection of the methoxy groups with BBr_3 (Scheme 3). The diol **6** was then protected with 1,2-bis(trimethylsiloxy)ethane. The resulting product **7**, isolated in 70% yield, proved only moderately stable and decomposed upon standing after a week. Undoubtedly, the presence of the mildly acidic phenolic protons was catalysing the attack on the acetal functionality. However, **7** could be kept indefinitely in solution (in THF) if stored over sodium carbonate. In practise, the compound was used immediately after preparation and purification.

The reaction between 4-fluoro-3′,5′-dihydroxybenzophenone and **7** proceeded in 73% yield to give a waxy amorphous solid **8**. Sodium carbonate was used as a base, as it has been reported that the use of potassium carbonate can catalyse transetherification reactions in similar systems.[17] This is because the bi-product, potassium fluoride, is soluble in DMSO solvent and can attack the existing diphenyl ketone ether structures, whereas sodium fluoride is insoluble. While this is of little consequence when producing polymers, in the present case any transetherification will produce scrambling of the dendrimer leading to defects in the structures. We looked at DMF as an alternative solvent. However, at high temperatures needed for the coupling, we found some



Scheme 2.



Scheme 3. Synthesis of generation one dendron **9**.

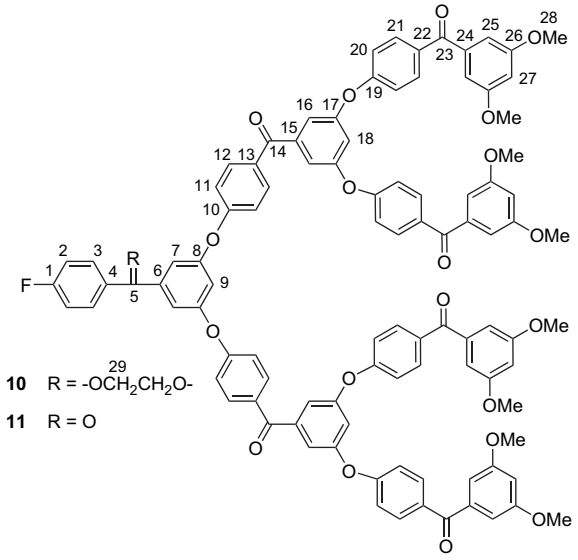
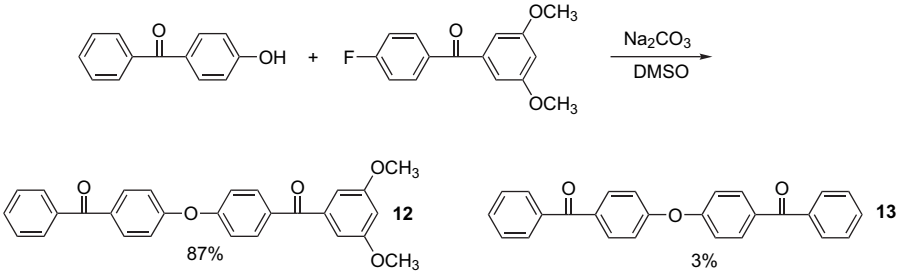


Figure 1. Structure and atom numbering of dendrons **10** and **11**.

substitution of fluoride with dimethylamine had occurred. This side-product, probably arose via decomposition of the solvent under the basic conditions.

The NMR of **8** showed that the acetal ring survived during the reaction and work-up. Again, the reaction appeared clean with only one product seen on TLC analysis and isolated. Compound **8** was deprotected cleanly to give the first generation product **9**. Coupling of **9** with **7** under identical conditions as before gave the protected second generation wedge **10** in a reduced yield of 48% (Fig. 1). Unlike previous couplings, several other compounds could be seen under TLC analysis, suggesting that the reaction was not quite as clean as hoped. Deprotection as before gave **11** in 83% yield as an amorphous white solid. While the deprotection was very clean by TLC analysis, some of the compounds appeared to irreversibly bind to the silica column, perhaps accounting for the less than quantitative yields.

Attempted preparation of the third generation wedge produced a complex mixture that couldn't be purified further. It was obvious that side reactions were competing with the desired coupling reactions. In order to determine the possible cause, a model study was performed. Coupling of 4-hydroxybenzophenone with **1**, under conditions used previously, gave an isolated yield of 87% of the expected product **12**, along with 3% of the side-product **13**. The side-product was clearly being produced by the attack of phenoxide on the product (Scheme 4). Transetherification in benzophenone derivatives has been noted before,[17] and we were unable to find any different conditions (temperature, solvents or base) to eliminate the formation of this side-product. It appears that the rate difference in the nucleophilic aromatic substitution between an aryl fluoride and aryl phenyl ether



Scheme 4. Model coupling reaction.

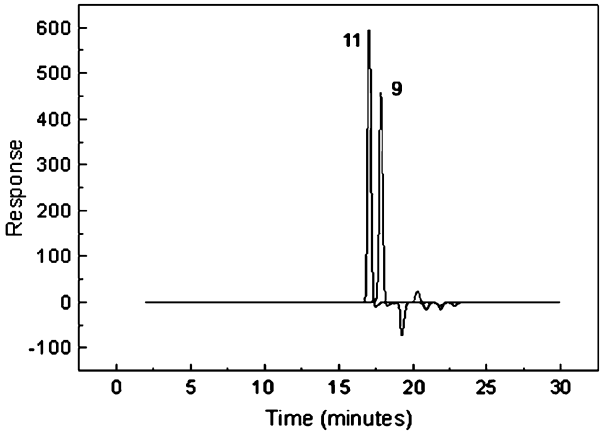


Figure 2. Size exclusion chromatographs of dendrons **9** and **11**.

may be fairly insensitive to conditions. Three percent transetherification is of minor consequence in the formation of lower generation dendrimers. However, by the time a generation three product is required, there are six times more potentially reactive aryl ether sites than fluoride sites in the starting material. Added to this is the strong possibility that the terminal fluoride group may have lower reactivity than expected due to steric crowding at the apex of the dendron. The net result appears to be the scrambling of dendrimeric structure at high generation, which appears to be a limitation in the use of a nucleophilic route to higher poly(phenyl ether) structures at present.

The purity of the generations one and two wedges was checked for any scrambling. The ^{1}H and ^{13}C NMR spectra of both products were very clean, and all the carbons could be accounted for, with no extra peaks. The carbon and proton spectra were fully assigned by use of model compounds and peak intensities. Gel permeation chromatography of the generations one and two structures showed a monodisperse product (polydispersity$<$1.05) (Fig. 2), and mass spectral analysis (ESI) showed no higher molecular weight products. The dendrimers were all amorphous, waxy materials, perhaps suggesting a low T_g for the un-cross-linked material. DSC measurements did not reveal an obvious glass transition point, perhaps due to the variety of the structural elements present.

3. Conclusions

Protection of an aryl fluoride towards nucleophilic substitution can be achieved via acetylisation of a *para*-ketone substituent. The best reagent for the protection was found to be trimethylsilyl trifluoromethanesulfonate. Deprotection can be achieved under mild acidic conditions to activate the fluoro-group. This protection–deprotection strategy allows the formation of phenyl ketone denritic wedges and possibly dendrimers to be constructed in a convergent fashion. A generation two dendritic wedge was ultimately constructed. This method works well for lower generations, but transetherification produces scrambling at higher generation that limits the utility of this method at this time for larger structures until more selective reaction conditions are found.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded using Bruker DPX-250 (250 MHz), DPX-400 (400 MHz) and DPX-500 (500 MHz) using the indicated deuterated solvent. Chemical shifts (δ in parts per million) are quoted relative to residual proton signals in chloroform where δ ($CHCl_3$)=7.26. Signal multiplets are quoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Infrared spectra were recorded on a Nicolet 510 FT-IR spectrometer. The samples were prepared as KBr discs or as thin films on NaCl plates as an oil. Microanalysis was performed by the University Chemical Laboratory Microanalytical Department. Melting points were determined using a Gallenkamp melting point apparatus and are not corrected. Flash chromatography was carried out on Merck Silica Gel 60. Thin layer chromatography (TLC) was carried out on a pre-coated 0.2 mm Merck 60 F_{254} silica plates, visualised by either UV light (366 nm) or potassium permanganate oxidation. Size exclusion chromatography was carried out using 3 Polymer Laboratories PL Gel mixed C (cross-linked polystyrene/divinylbenzene) columns, chloroform solvent, flow rate 1 mL/min and at 30 °C.

4.1.1. 4-(2-Phenyl-[1,3]dioxolan-2-yl)-phenol (2). To a solution of 4-hydroxybenzophenone **1** (0.60 g, 3.0 mmol) in dry DCM (15 mL), at 0 °C under nitrogen, was added 1,2-bis(trimethylsilyloxy)ethane (1.40 mL, 6.1 mmol). The mixture was left for 30 min under nitrogen and then trimethylsilyl trifluoromethanesulfonate (0.06 mL, 0.3 mmol) was added under nitrogen. After 30 min the temperature was raised to room temperature for 5 h. Pyridine (0.1 mL) was added to the mixture and then it was placed into water (40 mL) and extracted with ethyl acetate (3×30 mL). The combined extracts were then dried over magnesium sulfate, filtered and concentrated in vacuo. Column chromatography on silica gel, using 82:18 hexane/ethyl acetate yielded 0.52 g (71%) of a white solid, **2**; R_f (hexane/ethyl acetate 1:1) 0.85; mp 107–109 °C; IR (KBr) 3100–3000, 2900, 1590, 1555, 1500, 1250, 1180 cm^{-1}; ^{1}H NMR (400 MHz) δ ($CDCl_3$) 7.49 (d, 2H, H-3, $^{3}J_{HH}$=8.0 Hz), 7.37–7.25 (m, 5H, aromatic), 6.74 (d, 2H, H-8, $^{3}J_{HH}$=9.0 Hz), 4.93 (s, 1H, OH), 4.04 (m, 4H, H-10); *m/z* (ESI) 265.08 [M+Na^+. $C_{15}H_{14}O_3Na$ requires M+Na, 265.08406]; *m/z* (ESI) 265.1 (M+Na^+, 100%), 243.1 (23%); found C, 74.0%; H, 5.8%. $C_{15}H_{14}O_3$ requires C, 74.4%; H, 5.8%.

4.1.2. Phenyl-4-{[4-(2-phenyl-[1,3]dioxolan-2-yl)-phenoxy]-phenyl}-methanone (3). To a solution of compound **2** (0.50 g, 2.1 mmol) and 4-fluorobenzophenone (0.46 g, 2.1 mmol) in dry DMSO (20 mL) was added Na_2CO_3 (0.22 g, 2.1 mmol). The mixture was heated to 160 °C for 24 h and then cooled to room temperature. Water (40 mL) was then added and the mixture was extracted with ethyl acetate (3×30 mL). The combined extracts were then dried over magnesium sulfate, filtered and concentrated in vacuo. Recrystallisation from hexane/ether yielded 0.72 g (84%) of a white solid, **3**; R_f (hexane/ethyl acetate 1:1) 0.69; mp 119–121 °C; IR (KBr) 3050, 2900, 1660, 1590, 1310, 1250, 1180, 1080 cm^{-1}; ^{1}H NMR (400 MHz) δ ($CDCl_3$) 7.79 (d, 2H,

H-16, $^3J_{HH}$=7.0 Hz), 7.76 (d, 2H, H-12, $^3J_{HH}$=7.0 Hz), 7.58–7.50 (m, 4H, aromatic), 7.45 (t, 2H, H-2, $^3J_{HH}$= 8.0 Hz), 7.36–7.27 (m, 4H, aromatic), 7.04 (d, 2H, H-8, $^3J_{HH}$=7.0 Hz), 7.01 (d, 2H, H-11, $^3J_{HH}$=7.0 Hz), 4.07 (m, 4H, H-19, H-20); ^{13}C NMR (100 MHz) δ ($CDCl_3$) 195.5, 161.3, 155.4, 141.9, 138.4, 137.9, 132.4, 132.1, 132.0, 129.8, 128.2, 128.2, 128.1, 126.1, 119.6, 117.3, 109.1, 64.9; *m/z* (EI) 422.15206 [M^+. $C_{28}H_{22}O_4$ requires M, 422.15181]; *m/z* (EI) 422.2 (M^+, 40%), 345.1 (100%), 149.1 (57%), 68.9 (38%); found C, 79.6%; H, 5.3%. $C_{28}H_{22}O_4$ requires C, 79.4%; H, 5.3%.

4.1.3. Bis-(4-benzoylphenyl) ether (4). To a solution of **3** (0.50 g, 1.2 mmol) in acetone (15 mL) was added *p*-toluenesulfonic acid (0.33 g, 1.2 mmol). The mixture was heated at 50 °C for 3 h and then placed in water (30 mL). The mixture was then extracted with ethyl acetate (3×30 mL). The combined extracts were then dried over magnesium sulfate, filtered and concentrated in vacuo. Recrystallisation from ethanol yielded 0.42 g (93%) of a white solid, **4**; R_f (hexane/ethyl acetate 1:1) 0.72; mp 162–164 °C (lit.[18] mp 163–165 °C); IR (KBr) 3030, 1650, 1600, 1500, 1320, 1290, 1170 cm^{-1}; ^{1}H NMR (400 MHz) δ ($CDCl_3$) 7.87 (d, 4H, H-7, $^3J_{HH}$=9.0 Hz), 7.79 (d, 4H, H-3, $^3J_{HH}$=7.0 Hz), 7.58 (t, 2H, H-1, $^3J_{HH}$=7.5 Hz), 7.48 (t, 4H, H-2, $^3J_{HH}$=7.5 Hz), 7.14 (d, 4H, H-8, $^3J_{HH}$=9.0 Hz); *m/z* (EI) 378.12547 [M^+. $C_{26}H_{18}O_3$ requires M, 378.12559]; *m/z* (EI) 378.1 (M^+, 98%), 301.1 (100%), 68.9 (97%); found C, 82.3%; H, 4.8%. $C_{26}H_{18}O_3$ requires C, 82.5%; H, 4.8%.

4.1.4. 5-(2-Phenyl-[1,3]dioxolan-2-yl)-benzene-1,3-diol (7). To a solution of 4-fluoro-3′,5′-dihydroxybenzophenone[10c] **6** (1.10 g, 4.7 mmol) in dry ether (15 mL), at 0 °C under nitrogen, was added 1,2-bis(trimethylsilyloxy)-ethane (1.40 mL, 6.1 mmol). The mixture was left for 30 min under nitrogen and then trimethylsilyl trifluoromethanesulfonate (0.06 mL, 0.3 mmol) and trifluoroacetic acid (two drops) were added. After 30 min, the temperature was raised to room temperature for 5 h. Pyridine (0.1 mL) was added to the mixture and, after 30 min, water (40 mL) was added. The mixture was extracted with ethyl acetate (3× 30 mL). The combined extracts were then dried over magnesium sulfate, filtered and concentrated in vacuo. Column chromatography on silica gel using 60:40 hexane/ethyl acetate yielded a waxy solid. The waxy solid was stirred in DCM where upon a precipitate was formed. The precipitate was filtered and the filtrate was concentrated in vacuo to yield 0.93 g (70%) of a waxy solid, **7**; R_f (hexane/ethyl acetate 1:1) 0.40; IR (KBr) 3100–3000, 2900, 1720, 1600, 1650, 1510, 1500, 1420, 1225, 1180 cm^{-1}; ^{1}H NMR (400 MHz) δ ($CDCl_3$) 7.45 (dd, 2H, H-3, $^3J_{HH}$=9.0 Hz, $^4J_{HF}$=9.0 Hz), 6.98 (t, 2H, H-2, $^3J_{HH}$=$^4J_{HF}$=9.0 Hz), 6.54 (d, 2H, H-7, $^4J_{HH}$=2.5 Hz), 6.26 (d, 1H, H-9, $^4J_{HH}$=2.5 Hz), 5.00–4.85 (s, 2H, OH), 4.04 (m, 4H, H-10, H-11); *m/z* (EI) 276.1 (M^+, 38%), 181.1 (45%), 167.1 (54%), 123.0 (54%), 95 (71%), 68.9 (100%); found C, 65.3%; H, 4.1%. $C_{15}H_{13}O_4F$ requires C, 65.2%; H, 4.7%.

4.1.5. First generation protected poly(ether ketone) dendron (8). 4-Fluoro-3′,5′-dimethoxybenzophenone[18] **5** (0.44 g, 1.6 mmol) and **7** (0.11 g, 0.8 mmol) were dissolved in dry DMSO (10 mL) and Na_2CO_3 (0.20 g) was added. The mixture was heated to 160 °C for 24 h and then cooled to room temperature. The solvent was evaporated and column chromatography on silica gel using 73:27 hexane/ethyl acetate yielded 0.43 g (72%) of a waxy solid, **8**; R_f (hexane/ethyl acetate 1:1) 0.60; IR (KBr) 2900, 1725, 1600, 1505, 1480, 1380, 1160, 1100 cm^{-1}; ^{1}H NMR (400 MHz) δ ($CDCl_3$) 7.81 (d, 4H, H-12, $^3J_{HH}$=8.8 Hz), 7.45 (m, 2H, H-3), 7.09–6.08 (m, 8H, H-7, H-2, H-11), 6.87 (d, 4H, H-16, $^3J_{HH}$=2.3 Hz), 6.71 (t, 1H, H-9, $^4J_{HH}$=2.3 Hz), 6.65 (t, 2H, H-18, $^4J_{HH}$=2.3 Hz), 4.05 (m, 4H, H-20), 3.82 (s, 12H, H-19); ^{13}C NMR (100 MHz) δ ($CDCl_3$) 195.0 (C14), 162.6 (d, J_{CF}=246 Hz, C1), 160.6 (C17, C10), 156.9 (C8), 146.4 (C6), 137.8 (C4), 132.5 (C12), 132.5 (C13), 127.8 (d, J_{CF}=9 Hz, C3), 117.9 (C11), 115.3 (d, J_{CF}=21 Hz, C2), 113.4 (C7), 110.8 (C9), 108.3 (C5), 107.7 (C16), 104.5 (C18), 65.1 (C20), 55.6 (C19); *m/z* (ESI) 779.22780 [M+Na^+. $C_{45}H_{37}O_{10}F$ requires M+Na, 779.22685]; *m/z* (ESI) 779.23 (M+Na^+, 100%); found C, 71.9%; H, 4.8%. $C_{45}H_{37}O_{10}F$ requires C, 71.5%; H, 4.9%.

4.1.6. Deprotected first generation poly(ether ketone) dendron (9). To the methoxy terminated poly(ether ketone) dendron **8** (0.27 g, 0.35 mmol) in acetone (10 mL) was added *p*-toluenesulfonic acid (0.2 g). The mixture was heated at 50 °C for 3 h and then placed in water (30 mL). The mixture was then extracted with ethyl acetate (3×30 mL). The combined extracts were then dried over magnesium sulfate, filtered and concentrated in vacuo. Column chromatography on silica gel using 75:25 hexane/ethyl acetate yielded 0.21 g (83%) of a waxy solid, **9**; R_f (hexane/ethyl acetate 1:1) 0.67; IR (KBr) 3000, 2810, 1725, 1655, 1600, 1505, 1480, 1280, 1170, 1080 cm^{-1}; ^{1}H NMR (400 MHz) δ ($CDCl_3$) 7.85 (m, 6H, H-3, H-12), 7.27 (d, 2H, H-7, $^4J_{HH}$=2.0 Hz), 7.16 (t, 2H, H-2, $^3J_{HH}$=$^3J_{HF}$=8.5 Hz), 7.09 (d, 4H, H-11, $^3J_{HH}$=8.5 Hz), 7.03 (t, 1H, H-9, $^4J_{HH}$=2.0 Hz), 6.87 (d, 4H, H-16, $^4J_{HH}$=2.5 Hz), 6.65 (t, 2H, H-18, $^4J_{HH}$=2.5 Hz), 3.82 (s, 12H, H-19); ^{13}C NMR (100 MHz) δ ($CDCl_3$) 194.9 (C14), 193.2 (C5), 165.5 (d, J_{CF}=254 Hz, C1), 160.6 (C17), 160.0 (C8), 157.4 (C10), 140.7 (C6), 139.5 (C15), 133.0 (C13), 132.9 (d, J_{CF}=3 Hz, C4), 132.7 (d, J_{CF}=9 Hz, C3), 132.6 (C12), 117.9 (C11), 116.2 (C7), 115.7 (d, J_{CF}=24 Hz, C2), 114.6 (C9), 107.7 (C16), 104.5 (C18), 55.6 (C19); *m/z* (EI) 735.20008 [M+Na^+. $C_{43}H_{33}O_9F$ requires M+Na, 735.20063]; *m/z* (ESI) 735.20 (M+Na^+, 30%), 306.1 (100%); found C, 72.7%; H, 5.2%. $C_{43}H_{33}O_9F$ requires C, 72.5%; H, 5.0%.

4.1.7. Second generation protected poly(ether ketone) dendron (10). Protected dendron **9** (0.20 g, 0.275 mmol) and diol **7** (0.038 g, 0.14 mmol) were dissolved in dry DMSO (7 mL) and Na_2CO_3 (0.12 g) was added. The mixture was heated to 160 °C for 24 h and then cooled to room temperature. Column chromatography on silica gel using 55:45 hexane/ethyl acetate yielded 0.11 g (48%) of a waxy solid, **10**; R_f (hexane/ethyl acetate 1:1) 0.52; IR (KBr) 3000, 2900, 1725, 1650, 1600, 1505, 1480, 1380, 1160, 1100, 1080 cm^{-1}; ^{1}H NMR (400 MHz) δ ($CDCl_3$) 7.87–7.79 (2d, 12H, H-12, H-21, $^3J_{HH}$=8.5 Hz), 7.43 (t, 2H, H-2, $^3J_{HH}$=$^3J_{HF}$=9.0 Hz), 7.26 (m, 4H, aromatic), 7.15–6.95 (m, 16H, aromatic), 6.87 (d, 8H, H-25, $^3J_{HH}$=2.0 Hz), 6.70 (m, 3H, H-18, H-9), 6.65 (t, 4H, H-27, $^4J_{HH}$=2.0 Hz), 4.03 (m, 4H, H-29, H-30), 3.80, (s, 24H, H-28); ^{13}C NMR (100 MHz) δ ($CDCl_3$) 194.9 (C23), 193.3 (C14), 164.6 (d, J_{C-F}= 151 Hz, C1), 161.4 (C10), 161.1 (C26), 160.6 (C19), 157.2

(C17), 156.7 (C8), 146.5 (C6), 141.0 (C15), 139.4 (C24), 132.9 (C22), 132.6 (C21), 132.5 (C12), 131.9 (C4), 131.5 (C13), 127.8 (d, J_{CF}=8 Hz, C3), 118.0 (C20), 117.6 (C11), 116.3 (C16), 115.2 (d, J_{CF}=21 Hz, C2), 114.4 (C7), 113.6 (C18), 111.1 (C9), 108.3 (C5), 107.7 (C25), 104.5 (C27), 65.1 (C29), 55.6 (C28); found C, 73.2%; H, 4.4%. $C_{101}H_{77}O_{22}F$ requires C, 73.0%; H, 4.7%.

4.1.8. Second generation deprotected poly(ether ketone) dendron (11). To the methoxy terminated poly(ether ketone) dendron **10** (0.11 g, 0.056 mmol) in acetone (10 mL) was added *p*-toluenesulfonic acid (0.1 g). The mixture was heated at 50 °C for 3 h and then placed in water (20 mL). The mixture was then extracted with ethyl acetate (3× 20 mL). The combined extracts were then dried over magnesium sulfate, filtered and concentrated in vacuo. Column chromatography on silica gel using 57:43 hexane/ethyl acetate yielded 0.09 g (80%) of a waxy solid, **11**; R_f (hexane/ethyl acetate 1:1) 0.54; IR (KBr) 2900, 1725, 1700, 1690, 1650, 1600, 1505, 1480, 1280, 1235, 1155, 1080 cm^{-1}; ^1H NMR (400 MHz) δ ($CDCl_3$) 7.85 (m, 14H, H-3, H-12, H-21), 7.27–7.23 (m, 7H, aromatic), 7.15–7.00 (m, 16H, aromatic), 6.87 (d, 8H, H-25, $^3J_{HH}$=2.3 Hz), 6.64 (t, 4H, H-27, $^4J_{HH}$=2.3 Hz), 3.80 (s, 24H, H-28); ^{13}C NMR (100 MHz) δ ($CDCl_3$) 194.9 (C23), 193.2 (C14), 193.0 (C5), 160.6 (C26), 160.5 (C10), 160.1 (C19), 157.3 (C17), 157.1 (C8), 140.9 (C15), 140.8 (C6), 139.5 (C24), 133.0 (C22), 132.7 (C21+C12+C3), 132.6 (C4), 132.1 (C13), 118.0 (C11), 117.9 (C20), 116.5 (C7), 116.4 (C16), 115.7 (d, J_{CF}=18 Hz), 114.8 (C9), 114.5 (C18), 107.7 (C25), 104.5 (C27), 55.6 (C28); SEC (THF) M_w 1210, PD 1.05; found C, 73.0%; H, 5.3%. $C_{99}H_{73}O_8F$ requires C, 73.4%; H, 4.8%.

4.1.9. {4-[4-(3,5-Dimethoxy-benzoyl)-phenoxy]-phenyl}-phenyl-methanone (12). To a solution of 4-fluoro-3′,5′-dimethoxybenzophenone **5** (0.20 g, 0.7 mmol) and 4-hydroxybenzophenone (0.15 g, 0.8 mmol) in anhydrous DMSO (20 mL) was added Na_2CO_3 (0.81 g, 0.8 mmol). The mixture was heated to 160 °C under nitrogen for 24 h and then cooled to room temperature. The mixture was then added to water (40 mL) and extracted with ethyl acetate (3×40 mL). The combined extracts were then dried over magnesium sulfate, filtered and concentrated in vacuo. Column chromatography on silica gel using 90:10 hexane/ethyl acetate yielded 0.30 g (89%) of product as a waxy solid, **12**; R_f (hexane/ethyl acetate 1:1) 0.82; IR (KBr) 2950, 2360, 1710, 1660, 1590, 1510, 1460, 1110 cm^{-1}; ^1H NMR (400 MHz) δ ($CDCl_3$) 7.87 (d, 2H, H-3, $^3J_{HH}$=9.0 Hz), 7.85 (d, 2H, H-7, $^3J_{HH}$=9.0 Hz), 7.78 (d, 2H, H-3, $^3J_{HH}$= 7.0 Hz), 7.58 (t, 1H, H-1, $^3J_{HH}$=7.5 Hz), 7.48 (t, 2H, H-2, $^3J_{HH}$=7.5 Hz), 7.12 (m, 4H, H-8, H-11), 6.90 (d, 2H, H-16, $^4J_{HH}$=2.5 Hz), 6.66 (t, 1H, H-18, $^4J_{HH}$=2.5 Hz), 3.82 (s, 6H, H-19); ^{13}C NMR (100 MHz) δ ($CDCl_3$) 195.4, 195.0 (C5, C14), 160.6 (C17), 159.9, 159.8 (C9, C10), 139.5 (C15), 137.7 (C4), 133.5, 133.1 (C6, C13), 132.5, 132.5 (C7, C12), 132.3 (C1), 131.9, (C3), 129.8, 128.3 (C2), 118.6, 118.5 (C8, C11), 107.8 (C16), 104.5 (C18), 55.6 (C19); *m/z* (EI) 438.14734 [M^+. $C_{28}H_{22}O_5$ requires M, 438.14673]; *m/z* (EI) 438.1 (30%), 301.1 (20%), 119.0 (80%), 68.8 (100%); found C, 77.1%; H, 5.7%. $C_{28}H_{22}O_5$ requires C, 76.7%; H, 5.1%.

Column chromatography using 85:15 hexane/ethyl acetate and crystallisation from ether/hexane yielded 0.009 g (3%) of a white solid, **4**.

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