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# Synthesis, characterisation, electronic spectra and electrochemical investigation of ferrocenyl-terminated dendrimers



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#### ABSTRACT

Two new dodecaferrocenyl dendrimers have been prepared using a sixfold Sonogashira coupling reaction and sixfold Huisgen cycloaddition, respectively. In addition, a dendron containing four ferrocenyl groups has been synthesised by conventional synthetic methods. Electrochemical studies have shown that all the ferrocene units are electrochemically equivalent. Moreover, when treated with acid these compounds form multicharged methylium near-infrared-absorbing dendritic dyes with a high extinction coefficient.

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#### 1. Introduction

Dendrimers are monodisperse hyperbranched macromolecules and with characteristic structural features: the core of the molecule, the branches spreading out from the core and the functional groups on the periphery. The properties of dendrimers are dominated by the tunable surface functional groups, which present the opportunity to develop novel functional materials for medicine, biology, chemistry, physics and engineering.

Dendrimers are excellent scaffolds for the attachment of chromophores at their peripheral positions and useful optical properties of dyes located on dendrimer shells have been described.<sup>1</sup>

Near-infrared (NIR) dyes, with absorption and/or emission in the spectral range 700–1400 nm, are of great interest because of their promising applications in biosensing probes, optical communication, photovoltaics, solar cells, etc. These dyes require a narrow HOMO–LUMO gap, which in organic materials is commonly achieved through extensive  $\pi$ -conjugated systems endcapped with strong electron donor and acceptor substituents.<sup>2</sup> Many of the so-called push–pull or D– $\pi$ –A systems (D=donor, A=acceptor) share applications in the fields of nonlinear optics (NLOs) and organic electronics. Ferrocene, an interesting compound widely used as standard in electrochemistry due to its reversible one-electron redox behaviour, has been used as the donor substituent in push—pull systems to generate NIR dyes not only by us,<sup>3</sup> but also by others,<sup>4</sup> while ferrocenyl-containing dendrimers have been widely described,<sup>5,6</sup> and promising applications include artificial enzymes, molecular batteries, sensors, photoswitchable hosts, etc. NIR dendrimers are also known,<sup>7</sup> but ferrocenyl NIR dendrimers are, to the best of our knowledge, only known where the ferrocene substituent is present in its oxidized ferrocenium state.<sup>7k</sup>

In this letter, we report the design and synthesis of two novel dodecaferrocenyl dendrimers using a sixfold Sonogashira coupling reaction and sixfold Huisgen cycloaddition that form multicharged methylium near-infrared-absorbing dendritic dyes when treated with acid.

#### 2. Results and discussion

#### 2.1. Synthesis

Initially, we had planned to prepare a dendrimer containing branches of type **I**, as an analogue of a ferrocene monomer<sup>3a</sup> previously synthesised by our group, which formed a stable crystalline NIR dye when treated with acid. Our proposed route to branches of this type was via addition of {2,6-dimethoxy-4-[2-(ferrocenyl) ethenyl]phenyl}lithium (**II**) to a suitable ester (Scheme 1).



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Because it was anticipated that carbocation formation could be a side reaction during branch manipulation, the attachment of the carbinol-containing branches was planned as a late step in the synthesis.

We initially synthesised a hypercore (5) lacking any functionalities sensitive and/or reactive to lithiation (apart from the reactive peripheral groups). This was prepared by Williamson etherification between 1,1,1-tris(4-hydroxyphenyl)ethane and bromide 4, the latter being prepared from ethyl 4-hydroxybenzoate in three steps and 58% overall vield (Scheme 2). However, the addition of **II** to core 5 lead to a mixture containing the starting materials and unidentified by-products and a convergent synthetic approach was attempted instead. Thus alcohol 3a was first silvlated, then reacted with **II** and the product deprotected to afford **7b**. Unfortunately, benzyl alcohol **7b** could not be transformed to the corresponding benzyl bromide using mild reaction conditions, e.g., CBr<sub>4</sub>/PPh<sub>3</sub>. The use of PBr<sub>3</sub> was ruled out due to the acid sensitivity of the carbinol functionalities. An alternative route via Mitsunobu reaction between **7b** and trimesic acid was also attempted but the starting materials were recovered and so an alternative dendrimer was designed.

We conceived a dendrimer containing acetylene functionalities between the core and the carbinol-containing branches (**16a**), which would increase the conjugation<sup>8</sup> of the chromophore units and present the possibility of dendrimer assembly through a Sonogashira coupling reaction. To this end, hypercore compound **8**, containing the iodo functionalities required for the carbon--carbon bond formation, was prepared by the condensation of trimesoyl chloride and benzyl alcohol **3b** (Scheme 3), the latter being prepared analogously to **3a** (see Scheme 2).

The acetylene-terminated ferrocenyl branch **12a**, required for the palladium-catalysed cross coupling reaction, was synthesized in 53% overall yield by addition of **II** onto ethyl 3trimethylsilylpropynoate<sup>9</sup> followed by in situ base-promoted desilylation (Scheme 4). However, the envisaged coupling between **8** and **12a** was unsuccessful. This unreactivity might have been due to the presence of too many electron donating substituents on the acetylenic branch<sup>10</sup> as a Sonogashira coupling was successfully achieved with 1,1-bis(4-((*E*)-2-ferrocenylethenyl)phenyl)prop-2-yn-1-ol (**12b**), 1,1-diphenylprop-2-yn-1-ol (**12c**) and 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (**12d**)<sup>11</sup> (Scheme 6) vide infra.

The modified acetylenic branch **12b** was synthesized from 4,4'bis(bromomethyl) benzophenone,<sup>12</sup> which was transformed to the corresponding bis-phosphonate (**14**) and then reacted with ferrocenecarboxaldehyde to generate ketone **15** in 49% yield as the only geometric isomer (two steps, Scheme 5). In the latter Horner Emmons reaction it was important to use an excess of the aldehyde and run the reaction at high dilution to avoid the formation of polymeric products. Ketone **15** was then converted to propynol **12b** by addition of lithium trimethylsilylacetylene with subsequent desilylation (Scheme 5). Finally a sixfold Sonogashira reaction between iodine hypercore **8** and acetylene branch **12b** gave dendrimer **16b** in 79% yield. Similarly, dendrimers **16c** and **16d** were obtained in 68% and 84% yield, respectively (Scheme 6).

Unexpectedly, when the ferrocenyl dendrimer **16b** was treated with trifluoroacetic acid, the generated carbocation species was found to be very unstable as the purple solution lost its colour within seconds of its preparation (vide infra). It was assumed that the instability was due to the presence of the triple bond despite the fact that smaller triarylmethane dye ethynylogues had been described to be fairly stable in aprotic solvents.<sup>8,13</sup> Only Matsui and co-workers have reported a remarkably unstable triarylmethane dye but its structure was not described.<sup>14</sup> An alternative dendrimer was therefore designed, which contained a triazole linkage that would be constructed using click chemistry methodology.<sup>15</sup>

Synthesis of dendrimer 20 (Scheme 8) required the hexaacetylene-terminated core 10, which was prepared via the three-fold esterification of 3,5-bis(2-propynyloxy)benzenemethanol  $9^{16}$  with trimesoyl chloride in the presence of DMAP (see Scheme 3). In order to prepare the azide-containing branch 18, bromide 2a was transformed to the corresponding azide and the product was treated with stilbenyllithium **19**<sup>3</sup> at low temperature (Scheme 7). In this last step it was important to keep the temperature low in order to avoid side reactions at the azido functionality, and for this reason the analogous reaction with {2,6-dimethoxy-4-[2-(ferrocenyl)ethenyl]phenyl}lithium (II) failed.<sup>17</sup> Finally, reaction of core 10 with 8 equiv of azide 18 under Cu(I)-catalyzed Huisgen 'click reaction' conditions using the organosoluble copper catalyst Cu(PPh<sub>3</sub>)<sub>3</sub>Br and microwave irradiation<sup>18</sup> was found to give the desired dendrimer 20 in 95% yield. Employing stoichiometric amount<sup>15</sup> (6.2 equiv) of azide **18** led to a dendrimer containing only 3 ferrocenyl branches as indicated by the integration of the signal corresponding to the heterocyclic proton in the <sup>1</sup>H NMR spectrum and the mass spectral measurement.

#### 2.2. Optical properties

The UV-visible absorption spectra were recorded in chloroform, both for the carbinols and for the corresponding triarylmethyl dyes generated by adding solutions of trifluoroacetic acid to solutions of the carbinols.

The absorptions at around 450 nm for the ferrocene containing carbinols (**7a**, **7b**, **16b** and **20**) are due to ferrocene d–d bands.<sup>19</sup> When this carbinols are treated with acid, carbocations are generated<sup>20</sup> and their electronic spectra exhibit an additional low-energy bands, one in the visible region ( $\lambda$ =540–600 nm), which



**Scheme 2**. Reagents and conditions: i, 1,4-dibromobutane, K<sub>2</sub>CO<sub>3</sub>, acetone, 56 °C (**2a**: 89%; **2b**: 89%); ii, 3,5-dihydroxybenzylalcohol, K<sub>2</sub>CO<sub>3</sub>, 18-crown-6 (or TBAI for **3b**), acetone, 56 °C (**3a**: 75%; **3b**: 93%); iii, CBr<sub>4</sub>, Ph<sub>3</sub>P, CH<sub>2</sub>Cl<sub>2</sub>, 25 °C (87%); iv, (1,1,1-tris(4-hydroxyphenyl)ethane, K<sub>2</sub>CO<sub>3</sub>, 18-crown-6, acetone, 56 °C (85%); v, TBSCl, imidazole, CH<sub>2</sub>Cl<sub>2</sub> rt (quant.); vi, **II**, Et<sub>2</sub>O, 35 °C (72%); vii, TBAF, THF, rt, 3 h (93%).

is assigned as charge transfer (CT) and another in the NIR region ( $\lambda$ =850–1025 nm) assigned as metal to ligand charge transfer (MLCT) (d $_{\pi}$ - $\pi^*$ ), processes, which are in accordance with Barlow's theoretical model.<sup>21</sup> These bands present both a bathochromic shift in respect to  $\pi$ -conjugated triphenylmethane dyes due to the lowering of the energy of the MLCT transitions in the ferrocenyl dyes.<sup>4c</sup> The broad MLCT band that appears in the NIR region shows a pH dependency, similar as the one found for smaller molecules;<sup>3</sup> as the acid concentration is increased, the NIR band gradually decreased (except for compound **20**). The disappearance of the NIR band at high acid concentration is attributed to the protonation of the iron atom of the ferrocenyl groups, which removes the

possibility of MLCT.<sup>22</sup> Similar pH dependency has been observed for dialkylamino terminated  $\pi$ -conjugated triphenylmethane dyes where *N*-protonation weakens and finally cancels the push–pull character of these carbacationic dyes.<sup>7a,23</sup>

The acid solution of carbinol **16b** was highly unstable and a rapid colour change (green, purple and brown successively) could be observed seconds after its preparation. This instability had not been anticipated based on known stable ethynologs of triphenylmethane dyes prepared by Akiyama<sup>9,13</sup> although it is known that propargylic alcohols rearrange in acidic conditions to  $\alpha$ , $\beta$ -unsaturated ketones.<sup>24</sup> By contrast, compound **16c** needed a couple of hours to react with the acid and turn blue.



Scheme 3. Reagents and conditions: i, benzene-1,3,5-tricarbonyl chloride, 3b or 9, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, 40 °C, 18 h (8: 90%; 10: 78%).



Scheme 4. Reagents and conditions: i, ethyl 3-trimethylsilylpropynoate, Et<sub>2</sub>O, 40 °C, 18 h; ii, KOH, MeOH, THF, 25 °C, 2 h (53% over two steps).



Scheme 5. Reagents and conditions: i, P(OEt)<sub>3</sub>, 156 °C, 3 h (65%); ii, FcCHO, NaH, THF, 66 °C, 30 min (76%); iii, (a) TMS-acetylene, *n*-BuLi, THF, -78 °C to rt, 18 h; (b) KOH, MeOH, rt, 1.5 h (85%).

Compound **20** behaved slightly differently and needed higher concentrations of acid in order to reach the maximum absorption of the NIR band. Once reached, this band also disappeared at lower pH. Presumably protonation of the multiple triazole rings occurs first and therefore a higher concentration of acid is required to achieve quantitative carbocation formation.

Carbocations obtained from dendrimers **16b** and **20** present an NIR band red-shifted with respect to branches **7a** and **7b**. This is

most probably due to the steric crowding around the central carbon atom that does not allow these dyes to achieve planarity.

#### 2.3. Electrochemical properties

The electrochemical properties of compounds **7a**, **16b** and **20** were investigated by CV with dichloromethane as solvent in the presence of *tert*-butylammonium perchlorate as the supporting



Scheme 6. Reagents and conditions: iv, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, Cul, Et<sub>3</sub>N, DMF, acetylene 150 °C, (16a: 0%, 16b: 79%, 16c: 68%, 16d: 84%).



Scheme 7. Reagents and conditions: i, NaN<sub>3</sub>, H<sub>2</sub>O/acetone,  $\Delta$ , 18 h (75%); ii, FcC<sub>2</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>Li (19), THF, -78 °C, 30 min (65%).

electrolyte, using graphite rods as working and counter electrodes and an Ag/Ag<sup>+</sup> reference electrode at ambient temperature. The redox process was found to be very similar for the three compounds, which display a quasi-reversible one-electron redox wave attributed to the Fe(III)/Fe(II) redox couple ( $i_{ox}/i_{red} = \sim 1$ ), therefore indicating that the four (**7a**) and twelve (**16b** and **20**) ferrocene units are electrochemically equivalent. The redox potentials are summarized in Table 2.



Scheme 8. Reagents and conditions: i, Cu(PPh<sub>3</sub>)<sub>3</sub>Br, DIPEA, THF, MW, 140 °C, 20 min (95%).

Table 1Electronic spectra of carbinols and their carbenium ions

Compound	[Dye] M	[TFA] M	$\lambda_{Vis} (\log \epsilon)$	$\lambda_{\rm NIR} (\log \epsilon)$
7a	1.50E-4	_	453 (3.60)	
	1.50E-5	2.0E-4	594 (4.75)	858 (4.46)
	3.70E-5	5.2E-2	592 (4.68)	_
7b	1.8E-4	_	453 (371)	
	1.8E-5	5.2E-3	594 (4.79)	855 (4.50)
	1.8E-5	5.2E-2	600 (4.85)	865 (4.12)
	1.8E-5	1.0E-1	603 (4.77)	_
16b	2.1E-5	_	449 (4.25)	
	1.0E-5	1.3E-2	517 (3.63)	959 (4.5)
16c	4.2E-4	_	268 (3.80)	
	2.1E-5	2.6E-2	576 (4.96) <sup>a</sup>	
16d	1.0E-5	_	260 (5.16)	
	1.0E-5	3.9E-1	576 (5.25)	
20	5.0E-5	_	453 (4.19)	
20	5.0E-6	5.2E-2	544 (5.19)	999 (4.85)
	5.0E-6	2.6E-1	540 (5.44)	1024 (5.11)

<sup>a</sup> This band reached its maximum intensity in about 2 h after addition of the acid.

 Table 2

 Redox potentials of ferrocenyl dendrimers<sup>a</sup>

Entry	Compound	$\Delta E (mV)$	$E_0 (\mathrm{mV})$
1	7a	104	+61
2	16d	126	+58
3	20	765	+5

 $^a$  Experimental conditions: CH<sub>2</sub>Cl<sub>2</sub>; TBAP (0.1 M); concentration in electroactive compound:  $1\times 10^{-3}$  M; Ag/Ag^+ reference; 100 mV S $^{-1}$  sweep rate.

#### 3. Conclusions

In conclusion, dendrimers with ferrocenyl units at the surface were synthesised in good yields. The cyclic voltammetry studies revealed that they all undergo a reversible single electron transfer process. When treated with acid these dendrimers absorbed with a high extinction coefficient in the near-infrared area, although the dye derived from **16b** is very unstable.

#### 4. Experimental section

#### 4.1. General details

All reactions requiring dry or inert conditions were conducted in flame-dried equipment under an atmosphere of argon. Ethers were distilled from sodium-benzophenone: (chlorinated) hydrocarbons. amines, MeOH and DMF from CaH<sub>2</sub>. Reactions were monitored by TLC using commercially available Merck silica gel 60 F254 glassbacked plates. Visualisation of reaction components was achieved with a UV lamp (254 nm) and with anisaldehyde or KMnO<sub>4</sub> stains. Silica gel column chromatography was carried out on silica gel 60 (particle size 40-63 µm) as supplied by Merck. Size exclusion column chromatography was performed with Bio Beads<sup>®</sup> S-X1. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Varian 300 (300 MHz and 75 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively) or a Varian 600 (600 MHz and 150 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively). Chemical shifts are reported relative to the internal solvent [e.g.,  $\delta_{\rm H}$  7.27,  $\delta_{\rm C}$  (central line of t) 77.0 for CDCl<sub>3</sub>]. Coupling constants (J) are given in Hertz. Mass spectra were obtained using a Thermo Scientific LCQ Fleet (ESI) spectrometer. HRMS were determined by using a Thermo Scientific LTQ Orbitrap Velos (ESI) spectrometer. MALDI-TOF mass spectrometry was performed on a BRUKER DALTONICS REFLEX IV Matrix-Assisted Laser Desorption Ionization Time-Of-Flight spectrometer operating in linear mode using dithranol or 2,5dihydroxybenzoic acid as matrix. IR spectra were obtained on a Brucker ATR-IR spectrometer Model Tensor 27. UV-visible spectra were recorded on a Hitachi Model U-2001. Melting points (°C) are uncorrected.

Cyclic voltammograms (CV) were carried out using a PalmSense potentiostat (Palm Instruments, Houten, The Netherlands). The cyclic voltammetry was performed in a three-electrode standard cell, using graphite rod as working and counter electrodes and an  $Ag/Ag^+$  reference electrode. Measurements were conducted in  $CH_2Cl_2$  containing 100 mM Bu<sub>4</sub>NClO<sub>4</sub>. Solutions of the solutions of the ferrocenyl derivatives were 1 mM in concentration. The reference electrode was separated from the bulk solution by a fritted-glass bridge filled with 100 mM AgNO<sub>3</sub> solution.

Microwave reactions were carried out with a CEM Discover 300 W monomode microwave instrument. The closed vessels used were special glass tubes with self-sealing septa that controlled pressure with appropriate sensors on the top (outside the vial). The temperature was monitored through a non-contact infrared sensor centrally located beneath the cavity floor.

#### 4.2. Synthesis

4.2.1. Ethyl 4-(4-bromobutoxy)benzoate (**2a**).<sup>25</sup> Ethyl 4-hydroxybenzoate (2.5 g, 15.0 mmol) was added over a period of 15 min to a solution of 1,4-dibromobutane (13.0 g, 30.0 mmol) and K<sub>2</sub>CO<sub>3</sub> (4.2 g, 30.0 mmol) in acetone (50 mL) at 56 °C. The resulting mixture was heated at 56 °C for 4 h, then cooled, filtered, evaporated under reduced pressure and purified by column chromatography (20% CH<sub>2</sub>Cl<sub>2</sub> in hexane) to give bromo-ether **2a** (4.0 g, 13.28 mmol, 89%) as a white solid,  $R_f$  0.65 (50% Et<sub>2</sub>O in hexane);  $\nu_{max}$  2955, 1706, 1605, 1509, 1273, 1101, 769 cm<sup>-1</sup>;  $\delta_H$  (300 MHz, CDCl<sub>3</sub>) 8.00 (2H, d, *J* 8.9, 2× CH), 6.91 (2H, d, *J* 8.9, 2× CH), 4.36 (2H, q, *J* 7.1, OCH<sub>2</sub>CH<sub>3</sub>), 4.06 (2H, t, *J* 6.2, CH<sub>2</sub>O), 3.50 (2H, t, *J* 6.2, CH<sub>2</sub>Br), 2.07–1.97 (4H, m, CH<sub>2</sub>) and 1.37 (3H, t, *J* 7.1, CH<sub>3</sub>);  $\delta_C$  (75 MHz, CDCl<sub>3</sub>) 166.3 (C, quat.), 162.5 (C, quat.), 131.5 (CH), 122.9 (C, quat.), 113.9 (CH), 66.9 (CH<sub>2</sub>), 60.6 (CH<sub>2</sub>), 33.3 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 27.7 (CH<sub>2</sub>) and 14.4 (CH<sub>3</sub>).

4.2.2. Dendron **3a**. A mixture of bromide **2a** (4.0 g, 13.3 mmol), 3,5dihydroxybenzyl alcohol<sup>26</sup> (0.84 g, 6.0 mmol), K<sub>2</sub>CO<sub>3</sub> (2.9 g, 21.0 mmol) and 18-crown-6 (0.2 g, 0.7 mmol) in acetone (50 mL) was heated at 56 °C. After 48 h the reaction mixture was cooled, filtered, evaporated under reduced pressure and purified by column chromatography (100% CH<sub>2</sub>Cl<sub>2</sub>) to give *benzyl alcohol* **3a** (2.67 g, 75%) as a white solid, mp 91–93 °C;  $R_f$  0.28 (50% Et<sub>2</sub>O in hexane);  $\nu_{max}$  3526, 2963, 2987, 1712, 1604, 1245, 1164 cm<sup>-1</sup>;  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 7.99 (4H, d, *J* 8.9, 4× CH), 6.91 (4H, d, *J* 8.9, 4× CH), 6.52 (2H, d, *J* 2.1, 2× CH), 6.38 (1H, t, *J* 2.1, CH), 4.63 (2H, d, *J* 5.9, CH<sub>2</sub>OH), 4.53 (4H, q, *J* 7.1, 2× OCH<sub>2</sub>CH<sub>3</sub>), 4.10–4.00 (8H, m, 4× CH<sub>2</sub>O), 2.10–2.00 (8H, m, 4× CH<sub>2</sub>) and 1.39 (6H, t, *J* 7.1, 2× CH<sub>3</sub>);  $\delta_{\rm C}$  (75 MHz, CDCl<sub>3</sub>) 166.4 (C, quat.), 162.6 (C, quat.), 160.3 (C, quat.), 143.4 (C, quat.), 131.5 (CH), 122.8 (C, quat.), 113.9 (CH), 105.1 (CH), 100.5 (CH), 67.6 (CH<sub>2</sub>), 67.4 (CH<sub>2</sub>), 65.3 (CH<sub>2</sub>), 60.6 (CH<sub>2</sub>), 25.9 (CH<sub>2</sub>, two overlapping carbons) and 14.4 (CH<sub>3</sub>). MS (EI) *m*/*z*=603.29 ([M+Na]<sup>+</sup>, 100%). HRMS (ESI): [M+H]<sup>+</sup>, found 581.27582. C<sub>33</sub>H<sub>41</sub>O<sub>9</sub> requires 581.27451.

4.2.3. Dendron 4. A mixture of alcohol 3a (0.58 g, 1.0 mmol), carbon tetrabromide (0.46 g, 1.40 mmol) and triphenylphosphine (0.36 g, 1.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was stirred at 25 °C for 3 h. Then H<sub>2</sub>O (15 mL) was added and the product extracted into CH<sub>2</sub>Cl<sub>2</sub> (3×15 mL), washed with brine (15 mL), dried and evaporated under reduced pressure. The crude product was purified by column chromatography (gradient elution: 100% CH<sub>2</sub>Cl<sub>2</sub> to 20% Et<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub>) to give *benzyl bromide* **4** (0.56 g, 87%) as a white solid, mp 88–90 °C; Rf 0.71 (80% Et<sub>2</sub>O in hexane); v<sub>max</sub> 2961, 1704, 1604, 1249, 1162, 766 cm  $^{-1}$ ;  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 7.98 (4H, d, J 8.9, 4× CH), 6.91 (4H, d, J 8.9, 4× CH), 6.53 (2H, d, J 2.2, 2× CH), 6.38 (1H, t, J 2.2, CH), 4.40 (2H, s, CH<sub>2</sub>Br), 4.35 (4H, q, / 7.1, 2× OCH<sub>2</sub>CH<sub>3</sub>), 4.09 (4H, t, / 5.5, 2× CH<sub>2</sub>O), 4.02 (4H, t, / 5.5, 2× CH<sub>2</sub>O), 2.00–1.96 (8H, m, 4× CH<sub>2</sub>) and 1.38 (6H, t, / 7.1,  $2 \times$  CH<sub>3</sub>);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 166.2 (C, quat.), 162.5 (C, quat.), 160.1 (C, quat.), 139.6 (C, quat.), 131.4 (CH), 122.7 (C, quat.), 113.9 (CH), 107.4 (CH), 101.3 (CH), 67.5 (CH<sub>2</sub>), 67.4 (CH<sub>2</sub>), 60.5 (CH<sub>2</sub>), 33.5 (CH<sub>2</sub>), 25.8 (CH<sub>2</sub>), 25.7 (CH<sub>2</sub>) and 14.3 (CH<sub>3</sub>). ESI mass spectrum: MS (EI) *m*/*z*=642.79/644.77 (1:1) ([M]<sup>+</sup>, 100%), 550.82 (85), 246.84 (95). HRMS (ESI): [M+H]<sup>+</sup>, found 643.18836. C<sub>33</sub>H<sub>40</sub>Br<sup>79</sup>O<sub>8</sub> requires 643.19011.

4.2.4. Hypercore 5. A mixture of bromide 4 (1.8 g, 2.79 mmol), 1,1,1-tris(4-hydroxyphenyl)ethane (0.24 g, 0.79 mmol), K<sub>2</sub>CO<sub>3</sub> (0.87 g, 6.3 mmol) and 18-crown-6 (0.02 g, 0.07 mmol) in acetone (50 mL) was heated at 56 °C. After 20 h the reaction mixture was cooled, filtered, evaporated under reduced pressure and purified by size exclusion column chromatography (100% CH<sub>2</sub>Cl<sub>2</sub>) to give a glassy solid, *core* **5** (1.34 g, 85%); *R*<sub>f</sub> 0.41 (40% EtOAc in hexane);  $v_{\rm max}$  2953, 1706, 1604, 1508, 1249, 1165, 770 cm<sup>-1</sup>;  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 7.99 (12H, d, J 8.8, 12× CH), 7.01 (6H, d, J 8.5, 6× CH), 6.91 (12H, d, J 8.8, 12× CH), 6.86 (6H, d, J 8.5, 6× CH), 6.58 (6H, s,  $6\times$ CH), 6.40 (3H, s, 3× CH), 4.95 (6H, s, CH<sub>2</sub>), 4. 35 (12H, q, J 7.1, 6× OCH<sub>2</sub>CH<sub>3</sub>), 4.15-3.95 (24H, m, 12× CH<sub>2</sub>O), 2.11 (3H, s, CH<sub>3</sub>), 2.10–1.95 (24H, m, 12× CH<sub>2</sub>) and 1.38 (18H, t, J 7.1, 6× CH<sub>3</sub>);  $\delta_{\rm C}$ (75 MHz, CDCl<sub>3</sub>) 166.3 (C, quat.), 162.6 (C, quat.), 160.3 (C, quat.), 156.7 (C, quat.), 142.0 (C, quat.), 139.5 (C, quat.), 131.5 (CH), 129.6 (CH), 122.8 (C, quat.), 113.9 (CH, two overlapping carbons), 105.8 (CH), 100.7 (CH), 69.9 (OCH<sub>2</sub>), 67.6 (OCH<sub>2</sub>), 67.4 (OCH<sub>2</sub>), 60.6 (CH<sub>2</sub>), 50.6 (C, quat.), 30.7 (CH<sub>3</sub>), 25.9 (CH<sub>2</sub>), 25.8 (CH<sub>2</sub>) and 14.3 (CH<sub>3</sub>). MALDI mass spectrum: calcd for C<sub>119</sub>H<sub>132</sub>NaO<sub>27</sub> [M+Na]<sup>+</sup>: 2015.88. Found: 2015.61.

4.2.5. Dendron **6**. A mixture of benzyl alcohol **3a** (4.4 g, 7.5 mmol), *tert*-butyldimethylsilyl chloride (2.3 g, 9.1 mmol) and imidazole (1.5 g, 22.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) was stirred at 25 °C. After 2 h the reaction mixture was filtered and the solution was washed with brine, dried and evaporated under reduced pressure to give *silyl ether* **6** (5.2 g, quant.) as a white solid, mp 85–86 °C; *R*<sub>f</sub> 0.6 (50% Et<sub>2</sub>O in hexane); *v*<sub>max</sub> 2953, 2857, 1728, 1604, 1162, 1057, 832 cm<sup>-1</sup>;  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 7.99 (4H, d, *J* 8.7, 4× CH), 6.90 (4H, d, *J* 8.7, 4× CH), 6.48 (2H, d, *J* 2.1, 2× CH), 6.32 (1H, t, *J* 2.1, CH),

4.66 (2H, s, CH<sub>2</sub>), 4.34 (4H, q, *J* 7.1,  $2 \times \text{OCH}_2\text{CH}_3$ ), 4.08 (4H, t, *J* 5.5,  $2 \times \text{CH}_2$ ), 4.01 (4H, t, *J* 5.5,  $2 \times \text{CH}_2$ ), 2.00–1.95 (8H, m,  $4 \times \text{CH}_2$ ), 1.39 (6H, t, *J* 7.1,  $2 \times \text{CH}_3$ ), 0.97 (9H, s, SiC(CH<sub>3</sub>)<sub>3</sub>) and 0.1 (6H, s, Si(CH<sub>3</sub>)<sub>2</sub>);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>) 166.3 (C, quat.), 162.6 (C, quat.), 160.0 (C, quat.), 143.9 (C, quat.), 131.4 (CH), 122.7 (C, quat.), 113.9 (CH), 104.2 (CH), 99.9 (CH), 67.6 (OCH<sub>2</sub>), 67.3 (OCH<sub>2</sub>), 64.8 (OCH<sub>2</sub>), 60.6 (CH<sub>2</sub>), 25.9 (CMe<sub>3</sub>), 25.9 (CH<sub>2</sub>), 25.8 (CH<sub>2</sub>), 18.3 (C, quat.), 14.3 (CH<sub>3</sub>) and -5.3 (SiMe<sub>2</sub>). MS (EI) *m*/*z*=717.38 ([M+Na]<sup>+</sup>, 100%). HRMS (ESI): [M+H]<sup>+</sup>, found 695.35995. C<sub>39</sub>H<sub>55</sub>O<sub>9</sub>Si requires 695.36099.

4.2.6. Dendron **7a**. To a solution of  $II^{3a}$  (20.0 mmol) in Et<sub>2</sub>O (100 mL) silyl ether 6 (1.75 g, 2.5 mmol) was added as a solid in portions. The mixture was then warmed to reflux. After 18 h NH<sub>4</sub>Cl (satd aq solution) (30 mL) was added and the solution was concentrated CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was added, the layers were separated, the aqueous layer extracted with  $CH_2Cl_2$  (2×50 mL) and the combined organic layer was dried, filtered and evaporated to give an orange solid. The crude was stirred in Et<sub>2</sub>O and the product was filtered and purified by size exclusion column chromatography (100% toluene). Silyl ether 7a was obtained as an orange solid  $(3.64 \text{ g}, 72\%), R_f 0.42 (2\% \text{ Et}_3 \text{N in CH}_2 \text{Cl}_2); \delta_H (600 \text{ MHz}, \text{acetone}-d_6)$ 7.33 (4H, d, J 8.8, 4× CH), 7.00 (4H, d, J 16.1, 4× CH=), 6.76 (4H, d, J 8.8, 4× CH), 6.75 (8H, s, 8× CH), 6.73 (4H, d, J 16.1, 4× CH=), 6.53 (2H, d, J 2.3, 2× CH), 6.41 (1H, t, J 2.3, CH), 6.22 (2H, s, 2× OH), 4.70 (2H, s, CH<sub>2</sub>O), 4.51 (8H, J 2.0,  $8 \times$  Fc–CH), 4.27 (8H, J 2.0,  $8 \times$ Fc-CH), 4.13 (20H, s, Fc-CH), 4.10-4.00 (8H, m, 4× CH<sub>2</sub>), 3.47  $(24H, s, 8 \times \text{ OCH}_3)$ , 1.95–1.93 (8H, m, 4× CH<sub>2</sub>), 0.95 (9H, s, SiC(CH<sub>3</sub>)<sub>3</sub>) and 0.11 (6H, s, Si(CH<sub>3</sub>)<sub>2</sub>);  $\delta_C$  (75 MHz, acetone- $d_6$ ) 162.2 (C, quat.), 160.3 (C, quat.), 158.8 (C, quat.), 145.9 (C, quat.), 143.7 (C, quat.), 138.9 (C, quat.), 129.8 (CH), 128.4 (CH=), 128.0 (CH), 127.9 (CH=), 114.1 (C, quat.), 106.4 (CH), 106.2 (CH), 101.5 (CH), 85.5 (C, quat.), 81.0 (C, quat.), 70.9 (CH), 70.7 (CH), 69.3 (OCH<sub>2</sub>), 69.1 (OCH<sub>2</sub>), 68.6 (CH), 66.4 (OCH<sub>2</sub>), 57.8 (OMe), 27.9 (CH<sub>2</sub>), 27.8 (CH<sub>2</sub>), 27.3 (SiCMe<sub>3</sub>), 19.9 (SiCMe<sub>3</sub>) and -4.0 (SiMe<sub>2</sub>). MALDI mass spectrum: calcd for C<sub>115</sub>H<sub>122</sub>Fe<sub>4</sub>O<sub>14</sub>Si [M–OH]<sup>+</sup>: 1978.60. Found: 1978.415.

4.2.7. Dendron 7b. TBAF (0.73 mL, 0.73 mmol; 1 M in THF) was added to a solution of silyl ether 7a (970 mg, 0.48 mmol) in THF (50 mL) and the resulting mixture was stirred at 25 °C for 3 h. Then the solution was concentrated and the product extracted into CH<sub>2</sub>Cl<sub>2</sub> (50 mL), washed with brine (20 mL), dried and evaporated. The crude was purified by size exclusion chromatography (100% CH<sub>2</sub>Cl<sub>2</sub>) and dendron **7b** was obtained as an orange solid (840 mg, 93%), mp 135–138 °C; *R*<sub>f</sub> 0.35 (2% Et<sub>3</sub>N in CH<sub>2</sub>Cl<sub>2</sub>); *v*<sub>max</sub> 3474, 2931, 1596, 1231, 1104, 815 cm $^{-1}$ ;  $\delta_{\rm H}$  (600 MHz, acetone- $d_6$ ) 7.32 (4H, d, J 8.9, 4× CH), 7.00 (4H, d, J 16.1, 4× CH=), 6.76–6.73 (12H, m, 12× CH), 6.73 (4H, d, J 16.1, 4× CH=), 6.54 (2H, d, J 2.1, 2× CH), 6.41 (1H, t, / 2.1, CH), 6.22 (2H, s, 2× OH), 4.55 (2H, d, / 6.0, CH<sub>2</sub>O), 4.51 (8H, / 1.7, 8× Fc-CH), 4.28 (8H, / 1.7, 8× Fc-CH), 4.13 (20H, s, Fc-CH), 4.10-4.00 (8H, m, 4× CH<sub>2</sub>), 3.47 (24H, s, 4× OCH<sub>3</sub>) and 1.95-1.93 (8H, m,  $4 \times$  CH<sub>2</sub>);  $\delta_{C}$  (75 MHz, acetone- $d_{6}$ ) 162.2 (C, quat.), 160.3 (C, quat.), 158.7 (C, quat.), 146.9 (C, quat.), 143.7 (C, quat.), 138.9 (C, quat.), 129.8 (C, quat.), 128.4 (CH=), 127.9 (CH=), 127.9 (C, quat.), 114.1 (CH), 106.6 (CH), 106.4 (CH), 101.5 (CH), 85.5 (C, quat.), 81.0 (C, quat.), 70.9 (CH), 70.7 (CH), 69.2 (OCH<sub>2</sub>), 69.0 (OCH<sub>2</sub>), 68.6 (CH), 65.6 (OCH<sub>2</sub>), 57.8 (OMe), 27.9 (CH<sub>2</sub>) and 22.4 (CH<sub>2</sub>). MALDI mass spectrum: calcd for C<sub>109</sub>H<sub>108</sub>Fe<sub>4</sub>O<sub>14</sub> [M–OH]<sup>+</sup>: 1864.51. Found: 1864.49. HRMS (ESI): [M+H]<sup>+</sup>, found 1864.51349. C<sub>109</sub>H<sub>108</sub>Fe<sub>4</sub>O<sub>14</sub> requires 1864.51313.

4.2.8. 1-(4-Bromobutoxy)-4-iodobenzene (**2b**).<sup>27</sup> 4-lodophenol (7.0 g, 31.82 mmol), 1,4-dibromobutane (27.5 g, 127.36 mmol) and  $K_2CO_3$  (8.8 g, 63.67 mmol) were stirred in acetone (200 mL) at 56 °C. After 12 h the reaction mixture was cooled, filtered, evaporated under reduced pressure and purified by column chromatography (100% hexane) to give *bromo-ether* **2b** (10.0 g, 28.17 mmol, 89%) as a white solid, mp 28–29 °C (lit.<sup>27</sup> 26–27 °C); *R*<sub>f</sub> 0.2 (100% hexane);  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 7.55 (2H, d, *J* 8.9, 2× CH), 6.67 (2H, d, *J* 8.9, 2× CH), 3.95 (2H, t, *J* 6.0, CH<sub>2</sub>O), 3.48 (2H, t, *J* 6.0, CH<sub>2</sub>Br), 2.10–2.01 (2H, m, CH<sub>2</sub>) and 1.97–1.88 (2H, m, CH<sub>2</sub>);  $\delta_{\rm C}$ (75 MHz, CDCl<sub>3</sub>) 158.7 (C, quat.), 138.2 (CH), 116.8 (CH), 82.7 (C, quat.), 66.9 (CH<sub>2</sub>), 33.3 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>) and 27.7 (CH<sub>2</sub>). MS (EI) *m*/ *z*: 353.82 (100%), 355.82 (85).

4.2.9. Dendron 3b. A mixture of bromide 2b (8.6 g, 24.22 mmol), 3,5-dihydroxybenzyl alcohol<sup>26</sup> (1.2 g, 8.56 mmol), K<sub>2</sub>CO<sub>3</sub> (4.7 g, 34.01 mmol) and TBAI (0.1 g, 0.27 mmol) in acetone (100 mL) was heated at 56 °C. After 48 h the reaction mixture was cooled, filtered, evaporated under reduced pressure and purified by column chromatography (30% EtOAc in hexane) to give *benzyl alcohol* **3b** (5.49 g, 93%) as a white solid, mp 73–74 °C;  $R_f$  0.22 (30% EtOAc in hexane);  $\nu_{\rm max}$  3320, 2925, 2872, 1584, 1241, 1164, 815 cm<sup>-1</sup>;  $\delta_{\rm H}$  (600 MHz, CDCl<sub>3</sub>) 7.54 (4H, d, J 6.2, 4× CH), 6.67 (4H, d, J 6.2, 4× CH), 6.50 (2H, d, J 2.1, 2× CH), 6.35 (1H, t, J 2.1, CH), 4.61 (2H, s, CH<sub>2</sub>OH), 4.02–3.95 (8H, m,  $4 \times$  CH<sub>2</sub>O) and 1.97–1.93 (8H, m,  $4 \times$  CH<sub>2</sub>);  $\delta_{C}$  (150 MHz, CDCl<sub>3</sub>) 160.3 (C, quat.), 158.8 (C, quat.), 143.3 (C, quat.), 138.1 (CH), 116.9 (CH), 105.1 (CH), 100.5 (CH), 82.6 (CI), 67.50 (CH<sub>2</sub>), 67.4 (CH<sub>2</sub>), 65.3 (CH<sub>2</sub>), 25.9 (CH<sub>2</sub>) and 25.8 (CH<sub>2</sub>). MS (EI) *m*/*z*=505.20 (100%), 711 ([M+Na]<sup>+</sup>, 40). HRMS (ESI): [M+Na]<sup>+</sup>, found 711.00643. C<sub>27</sub>H<sub>30</sub>I<sub>2</sub>O<sub>5</sub>Na requires 711.00748.

4.2.10. Hypercore 8. A mixture of benzyl alcohol 3b (2.4 g, 3.47 mmol), benzene-1.3.5-tricarbonyl chloride<sup>28</sup> (265 mg. 1.00 mmol) and DMAP (423 mg, 3.47 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was heated at 40 °C. After 18 h the reaction mixture was cooled, filtered and evaporated under reduced pressure to give hypercore 8 (1.99 g, 90%) as a white solid, mp 93–94 °C;  $R_f$  0.41 (50% Et<sub>2</sub>O in hexane);  $v_{\rm max}$  2926, 2872, 1724, 1233, 1165, 814 cm<sup>-1</sup>;  $\delta_{\rm H}$  (600 MHz, CDCl<sub>3</sub>) 8.90 (3H, s, 3× CH), 7.51 (12H, d, J 8.5, 12× CH), 6.65 (12H, d, J 8.5, 12× CH), 6.56 (6H, s, 6× CH), 6.40 (3H, s, 3× CH), 5.30 (6H, s, 3× CH<sub>2</sub>), 4.05–3.90 (24H, m,  $12 \times$  OCH<sub>2</sub>) and 1.95–1.90 (24H, m,  $12 \times$ CH<sub>2</sub>); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>) 164.7 (C, quat.), 160.3 (C, quat.), 158.8 (C, quat.), 138.1 (CH), 137.5 (C, quat.), 134.9 (CH), 131.2 (C, quat.), 116.8 (CH), 106.7 (CH), 101.2 (CH), 82.6 (C, quat.), 67.5 (OCH<sub>2</sub>, two overlapping carbons), 67.3 (OCH<sub>2</sub>), 25.9 (CH<sub>2</sub>) and 25.8 (CH<sub>2</sub>). MALDI mass spectrum: calcd  $[M+Na]^+$  for  $C_{90}H_{90}I_6NaO_{18}$ : 2243.029. Found: 2243.150.

4.2.11. 1,1-Bis(4-((E)-ferrocen-1-enyl)-2,6-dimethoxyphenyl)prop-2*yn-1-ol* (**12a**). To a solution of stilbenyllithium **II**<sup>3a</sup> (10.0 mmol) in Et<sub>2</sub>O (100 mL) was added silyl ether 11<sup>9</sup> (440 mg, 2.57 mmol) in THF (20 mL). The mixture was then warmed to reflux. After 18 h NH<sub>4</sub>Cl (satd aq solution) (30 mL) was added and the solution was concentrated. CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was added, the layers were separated, the aqueous layer extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×50 mL) and the combined organic layers were dried, filtered and evaporated to give an orange solid. The crude was dissolved in THF (20 mL), a solution of KOH (190 mg, 3.3 mmol) in MeOH (4 mL) was added and the reaction mixture was then stirred at 25 °C. After 2 h the solvent was evaporated and the product was extracted into  $CH_2Cl_2$  (2×50 mL), washed with brine, dried, filtered and purified by size exclusion column chromatography (100% CH<sub>2</sub>Cl<sub>2</sub>). Acetylene 12a was obtained as an orange solid (1.02 g, 53%), mp 135–138 °C; Rf 0.17 (100% CH<sub>2</sub>Cl<sub>2</sub>);  $\nu_{max}$  3447, 3293, 2930, 2162, 1634, 1598, 1118, 812 cm<sup>-1</sup>;  $\delta_{\rm H}$ (600 MHz, CDCl\_3) 7.00 (1H, s, OH), 6.80 (2H, d, J 16.1), 6.63 (4H, s,  $4 \times$ CH), 6.60 (2H, d, J 16.1), 4.44 (4H, t, J 1.8, 4× Fc-CH), 4.28 (4H, t, J 1.8,  $4 \times$  Fc-CH), 4.14 (10H, s,  $10 \times$  Fc-CH), 3.76 (12H, s,  $4 \times$  OMe) and 2.68 (1H, s, CH); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>) 157.7 (C, quat.), 137.5 (C, quat.), 126.9 (CH=), 125.8 (CH=), 122.6 (C, quat.), 104.5 (CH), 88.2 (C, quat.), 83.1(C, quat.), 70.9 (C, quat.), 70.7 (CH), 69.2 (Fc-CH), 69.0 (Fc–CH), 66.8 (Fc–CH), 56.7 (OMe). MS (EI) m/z=419.44 (100%), 748.24 ([M]<sup>+</sup>, 75). HRMS (ESI): [M]<sup>+</sup>, found 748.15879. C<sub>43</sub>H<sub>40</sub>O<sub>5</sub>Fe<sub>2</sub> requires 748.15691.

4.2.12. 4.4'-Bisl(diethylphosphono)methyllbenzophenone (14). A mixture of 4,4'-dimethylbenzophenone (5 g, 23.8 mmol), NBS (9.3 g, 52.3 mmol) and AIBN (cat.) in CCl<sub>4</sub> (10 mL) was irradiated with a 275 W lamp for 1 h and then heated at 76 °C overnight. The reaction mixture was then cooled, filtered and evaporated under reduced pressure to give 4,4'-bis (bromomethyl) benzophenone<sup>12</sup> as a white solid;  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 7.79 (4H, d, I 8, 4× CH), 7.52 (4H d, J 8 4× CH) and 4.55 (4H, s, 2× OCH<sub>2</sub>Br). The crude dibromide was dissolved in triethyl phosphate (25 mL) and the mixture was heated at 150 °C for 3 h. The reaction mixture was then cooled and the unreacted phosphate and diethyl ethylphosphonate (formed during the reaction) were removed by vacuum distillation. Purification of the residue by column chromatography (gradient elution: 100% CH<sub>2</sub>Cl<sub>2</sub> to 6% MeOH in CH<sub>2</sub>Cl<sub>2</sub>) afforded phosphonate **14** as a yellow oil (7.45 g, 65%); *v*<sub>max</sub> 2982, 1713, 1654, 1243, 1017 cm<sup>-1</sup>;  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 7.74 (4H, d, J 8.0, 4× CH), 7.40 (4H, dd, J 8.0 and 2.5, 4× CH), 4.10-3.98 (8H, m, 4× OCH<sub>2</sub>CH<sub>3</sub>), 3.21 (4H, d, J 22.2, 2× CH<sub>2</sub>) and 1.25 (12H, t, J 7.1, 4× OCH<sub>2</sub>CH<sub>3</sub>);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 195.6 (C, quat.), 136.5 (C, quat., d, J 6.5), 135.9 (C, quat., d, J 3.5), 130.1 (CH, d, J 3), 129.5 (CH, d, J 6.5), 62.1 (OCH<sub>2</sub>, d, J 7), 33.7 (PCH<sub>2</sub>, d, J 137.5) and 16.2 (CH<sub>3</sub>, d, J 6). MS (EI) *m*/*z*=505.31 ([M+Na]<sup>+</sup>, 100%). HRMS (ESI): [M]<sup>+</sup>, found 482.1625. C<sub>23</sub>H<sub>32</sub>O<sub>7</sub>P<sub>2</sub> requires 482.1623.

4.2.13. 4.4'-Bisl(E)-2-(ferrocenvlethenvl)lbenzophenone (15). A solution of ferrocenecarboxaldehyde (1.78 g, 8.32 mmol) in THF (25 mL) was added to a suspension of sodium hydride (210 mg, 5.2 mmol; 60% in mineral oil) in THF (5 mL) and the mixture was heated to 70 °C. Then, a solution of phosphonate 14 (500 mg, 1.04 mmol) in THF (25 mL) was slowly added over a period of 1 h. Upon completion of addition the reaction mixture was stirred at 70 °C for another 30 min and then MeOH (10 mL) was added and the solvent evaporated. The residue was redissolved into CH<sub>2</sub>Cl<sub>2</sub> (50 mL), washed with brine (20 mL), dried and evaporated. The crude mixture, containing the product and excess ferrocenecarboxaldehyde, was taken into Et<sub>2</sub>O (50 mL) and the insoluble portion was filtered. Ferrocenyl derivative 15 was obtained as an orange solid (480 mg, 76%), which was used without further purification in the next step;  $\nu_{\rm max}$  1633, 1592, 1176, 813, cm $^{-1}$ ;  $\delta_{\rm H}$ (300 MHz, CDCl<sub>3</sub>) 7.80 (4H, d, J 8.0, 4× CH), 7.53 (4H, d, J 8.0, 4× CH), 7.06 (2H, d, J 16.3, 2× CH), 6.76 (2H, d, J 16.3, 2× CH), 4.51 (4H, s, 4× Fc–CH), 4.34 (4H, s, 4× Fc–CH) and 4.17 (10H, s, 10× Fc–CH);  $\delta_C$ (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 195.6 (C, quat.), 142.5 (C, quat.), 136.3 (C, quat.), 131.1 (CH), 130.9 (CH=), 125.8 (CH), 125.1 (CH), 62.1 (OCH<sub>2</sub>, d, J 7), 83.1 (C, quat.), 70.1 (Fc-CH), 69.9 (Fc-CH) and 67.8 (Fc-CH). MS (EI) m/z=602.25 (M<sup>+</sup>, 100%). HRMS (ESI): [M]<sup>+</sup>, found 602.09814. C<sub>37</sub>H<sub>30</sub>Fe<sub>2</sub>O 602.10 requires 602.0995.

4.2.14. 1,1-Bis(4-((*E*)-ferrocen-1-enyl)phenyl)prop-2-yn-1-ol (**12b**). n-BuLi (0.85 M in methylcyclohexane, 8.3 mL, 7.9 mmol) was added dropwise to a solution of (trimethylsilyl)acetylene (830 mg, 8.5 mmol) in anhydrous THF (50 mL) at -78 °C. After 30 min at -78 °C a solution of ketone **15** (1.7 g, 2.8 mmol) in dry THF (50 mL) was added at -78 °C and the reaction mixture was then allowed to warm up to rt and stirred at that temperature overnight. Then, a solution of KOH (240 mg, 4.3 mmol) in MeOH (3 mL) was added and stirring was continued until TLC indicated that deprotection was complete (1.5 h). The solvent was then evaporated, the crude was taken into CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and the solution was washed with brine (20 mL), dried and evaporated to yield *prop-2-yn-1-ol* **12b** (1.50 g, 85%) as an orange solid, mp 209–211 °C;  $\nu_{max}$  3538, 3286, 1631, 804 cm<sup>-1</sup>;  $\delta_{\rm H}$  (600 MHz, CDCl<sub>3</sub>) 7.59 (4H, d, *J* 8.2, 4× CH), 7.45 (4H, d, J 8.2, 4× CH), 6.99 (2H, d, J 16.2, 2× CH), 6.78 (2H, d, J 16.2 2× CH), 4.53 (4H, t, J 2.0, 4× Fc–CH), 4.28 (4H, t, J 2.0, 4× Fc–CH), 4.12 (10H, s, 10× Fc–CH) and 3.36 (1H, s, 1CH);  $\delta_C$  (75 MHz, CDCl<sub>3</sub>) 145.4 (C, quat.), 139.0 (C, quat.), 128.2 (CH=), 127.2 (CH), 126.3 (CH), 126.2 (CH=), 88.0 (C, quat.), 84.4 (C, quat.), 76.35 (CH), 74.17 (C, quat.), 70.0 (Fc–CH), 69.9 (Fc–CH) and 67.8 (Fc–CH); MS (EI) m/z=628.25 ([M+Na]<sup>+</sup>, 100%). HRMS (ESI): [M]<sup>+</sup>, found 628.11315. C<sub>39</sub>H<sub>32</sub>Fe<sub>2</sub>O requires 628.12400.

4.2.15. General procedure for the Sonogashira cross coupling reaction. Dendrimer **16b**. An oven-dried vessel was charged with the aryl iodide (80 mg, 0.036 mmol), the terminal alkyne (157 mg, 0.25 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (9 mg, 0.0125, 5 mol %), and Cul (5 mg, 0.025 mmol, 10 mol %). The vessel was evacuated and backfilled with argon three times. To the vessel, degassed DMF (5 mL) and degassed triethylamine (1 mL) were added.

The mixture was stirred at 80 °C overnight. After filtration through Celite<sup>®</sup>, the solvent was evaporated and the resulting residue was taken into CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and washed with brine (15 mL). The organic layer was separated, dried and evaporated and the crude purified by size exclusion column chromatography (100% CH<sub>2</sub>Cl<sub>2</sub>) to give *dendrimer* **16b** as an orange solid (150 mg, 79%), mp >250 °C;  $\nu_{max}$  1725, 1595, 1241, 808 cm<sup>-1</sup>;  $\delta_{H}$  (600 MHz, CDCl<sub>3</sub>) 8.89 (3H, s, 3× CH), 7.63 (24H, d, J 7.5, 24× CH), 7.40 (36H, m, 36× CH), 6.86 (12H, d, J 16, 12× CH=), 6.81 (12H, d, J 8, 12× CH), 6.68 (12H, d, J 16, 12× CH=), 6.54 (6H, s, 6× CH), 6.40 (3H, s, 3× CH), 5.28 (6H, s, 3× CH<sub>2</sub>), 4.45 (24H, s, 24× Fc-CH), 4.27 (24H, s, 24× Fc-CH), 4.12 (60H, s, 60× Fc-CH), 4.00-3.96 (24H, s, 12× CH<sub>2</sub>) and 1.90-1.97  $(24H, s, 12 \times CH_2); \delta_C (75 \text{ MHz, CDCl}_3) 164.7 (C, quat.), 160.2 (C, c)$ quat.), 159.2 (C, quat.), 143.6 (C, quat.), 137.2 (C, quat.), 134.9 (CH), 133.2 (CH), 131.1 (C, quat.), 128.6 (C, quat.), 127.2 (CH=), 126.3 (CH), 125.6 (CH), 125.3 (CH=), 114.4 (CH), 114.3 (C, quat.), 106.7 (CH), 101.1 (CH), 90.3 (C, quat.), 87.1 (C, quat.), 83.1 (C, quat.), 74.5 (C, quat.), 69.1 (Fc-CH), 69.1 (Fc-CH), 67.4 (3× OCH<sub>2</sub>), 66.9 (Fc-CH), 25.8 (CH<sub>2</sub>) and 25.8 (CH<sub>2</sub>). MALDI mass spectrum: calcd for C<sub>324</sub>H<sub>276</sub>Fe<sub>12</sub>O<sub>24</sub>: 5221.25. Found: 5220.76.

4.2.16. Dendrimer 16c. This compound was prepared from 12c (190 mg, 0.91 mmol) and **7** (290 mg, 0.13 mmol) according to the general procedure for Sonogashira cross coupling reaction. The crude product was purified by size exclusion column chromatography (100% CH<sub>2</sub>Cl<sub>2</sub>) to give *dendrimer* **16c** as a light yellow solid (240 mg, 68%), mp 88–90 °C;  $\nu_{\rm max}$  1724, 1601, 1507, 1242, 1167, 696 cm<sup>-1</sup>;  $\delta_{\rm H}$  (600 MHz, acetone- $d_6$ )  $\delta$  8.85 (3H, s, 3× CH), 7.70 (24H, d, J 7.5, 24× CH), 7.41 (12H, d, J 8.8, 12× CH), 7.31 (24H, t, J 7.5, 24× CH), 7.22 (12H, t, J 7.5, 12× CH), 6.91 (12H, d, J 8.8, 12× CH), 6.65 (6H, d, J 2.0, 6× CH), 6.46 (3H, t, J 2.0, 3× CH), 5.64 (6H, s, 6× OH), 5.34 (6H, s,  $3 \times$  OCH<sub>2</sub>), 4.05–4.02 (24H, s,  $12 \times$  CH<sub>2</sub>) and 1.92–1.89 (24H, s, 12× CH<sub>2</sub>);  $\delta_{C}$  (75 MHz, acetone- $d_{6}$ ) 165.0 (C, quat.), 161.3 (C, quat.), 160.3 (C, quat.), 147.5 (C, quat.), 138.9 (C, quat.), 135.0 (CH), 133.8 (CH), 132.3 (C, quat.), 128.8 (CH), 0, 127.9 (CH), 5, 126.8 (CH), 115.5 (CH), 107.3 (CH), 101.7 (CH), 92.2 (C, quat.), 86.8 (C, quat.), 74.7 (C, quat.), 68.3 (OCH<sub>2</sub>), 68.2 (OCH<sub>2</sub>), 67.2 (C(O)OCH<sub>2</sub>), 26.58 (CH<sub>2</sub>) and 26.5(CH<sub>2</sub>). MALDI mass spectrum: calcd for C<sub>180</sub>H<sub>162</sub>O<sub>27</sub> [M+H<sub>2</sub>O]<sup>+</sup>: 2755.13. Found: 2755.88.

4.2.17. Dendrimer **16d**. This compound was prepared from **12d** (268 mg, 1 mmol) and **7** (317 mg, 0.14 mmol) according to the general procedure for Sonogashira cross coupling reaction. The crude product was purified by size exclusion column chromatography (100% CH<sub>2</sub>Cl<sub>2</sub>) to give *dendrimer* **16d** as a green solid (360 mg, 84%), mp 139–141 °C;  $\nu_{max}$  3467, 1595, 1561, 1232, 1104, 815 cm<sup>-1</sup>;  $\delta_{\rm H}$  (300 MHz, acetone-*d*<sub>6</sub>) 8.87 (3H, s, 3× CH), 7.55–7.52 (24H, br, 24× CH), 7.38–7.35 (12H, br, 12× CH), 6.85–6.50 (36H, m, 12× CH+24× CH), 6.53 (6H, s, 6× CH), 6.39 (3H, s, 3× CH), 5.27 (6H, s, 3× OCH<sub>2</sub>), 4.05–3.85 (24H, s, 12× CH<sub>2</sub>),

3.57 (36H, s, 12× OCH<sub>3</sub>) and 1.95–1.85 (24H, s, 12× CH<sub>2</sub>);  $\delta_{\rm C}$  (75 MHz, CDCl<sub>3</sub>) 164.7 (C, quat.), 160.2 (C, quat.), 159.1 (C, quat.), 158.8 (C, quat.), 137.8 (C, quat.), 137.5 (C, quat.), 134.8 (CH), 133.1 (CH), 131.1 (C, quat.), 129.3 (CH), 127.3 (CH), 5, 114.4 (CH), 106.7 (CH), 101.2 (CH), 90.8 (C, quat.), 87.7 (C, quat.), 74.1 (C, quat.), 67.5 (OCH<sub>2</sub>), 67.4 (OCH<sub>2</sub>), 67.3 (C(O)OCH<sub>2</sub>), 55.2 (OMe), 25.9 (CH<sub>2</sub>) and 25.8 (CH<sub>2</sub>); MALDI mass spectrum: calcd for C<sub>192</sub>H<sub>180</sub>O<sub>36</sub>: 3062.22. Found: 3062.146.

4.2.18. Ethyl 4-(4-azidobutoxy)benzoate (**17**). A solution of bromide **2a** (1.6 g, 5.3 mmol) and sodium azide (1.7 g, 26,6 mmol) in acetone (20 mL) and H<sub>2</sub>O (5 mL) was heated to 56 °C. After 18 h the mixture was concentrated, diluted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and washed with water (15 mL). The combined organic layer was dried, filtered and evaporated to give azide **17** as a clear oil (1.0 g, 75%);  $R_f$  0.51 (50% Et<sub>2</sub>O in hexane);  $\nu_{max}$  2979, 2093, 1707, 1605, 1247, 1166, 1021, 769 cm<sup>-1</sup>;  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 8.00 (2H, d, *J* 8.4, 2× CH), 6.91 (2H, d, *J* 8.4, 2× CH), 4.35 (2H, q, *J* 7.2, CH<sub>2</sub>O), 4.05 (2H, t, *J* 6.1, CH<sub>2</sub>O), 3.38 (2H, t, *J* 6.1, CH<sub>2</sub>N<sub>3</sub>), 1.96–1.75 (4H, m, 2× CH<sub>2</sub>) and 1.39 (3H, t, *J* 7.2, CH<sub>3</sub>);  $\delta_{\rm C}$  (75 MHz, CDCl<sub>3</sub>) 166.1 (C, quat.), 162.4 (C, quat.), 131.5 (CH), 122.8 (C, quat.), 113.8 (CH), 67.2 (OCH<sub>2</sub>), 60.4 (OCH<sub>2</sub>), 50.9 (N<sub>3</sub>CH<sub>2</sub>), 26.2 (CH<sub>2</sub>), 25.5 (CH<sub>2</sub>) and 14.2 (CH<sub>3</sub>); MS (EI) *m*/*z*=263.97 ([M]<sup>+</sup>, 100%). HRMS (ESI): [M+H]<sup>+</sup>, found 264.13473. C<sub>13</sub>H<sub>18</sub>N<sub>3</sub>O<sub>3</sub> requires 264.13427.

4.2.19. (4-(4-Azidobutoxy)phenyl)bis(4-((E)-ferrocen-1-enyl)phenyl) *methanol* (**18**). To a solution of **19**<sup>3</sup> (0.8 g, 2.18 mmol) in THF (20 mL) at -78 °C was added a solution of ester 17 (217 mg, 0.87 mmol) in THF (5 mL) and the resulting mixture was stirred at -78 °C for 30 min NH<sub>4</sub>Cl (satd aq solution) (15 mL) was then added and the solution was concentrated. CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added, the layers were separated, the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×20 mL) and the combined organic layers were dried, filtered and evaporated to give an orange solid. The crude was then purified by column chromatography (gradient elution: 10% ethyl acetate in hexane to 20% ethyl acetate in hexane) to give carbinol 18 as an orange solid (450 mg, 65%), mp 82–83 °C; *R*<sub>f</sub> 0.26 (10% ethyl acetate in hexane);  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 7.39 (4H, d, J 8.5, 4× CH), 7.27 (4H, d, J 8.5, 4× CH), 7.23 (2H, d, J 9.0, 2× CH), 6.88 (2H, d, J 16.1, 2× CH=), 6.85 (2H, d, J 9.0, 2× CH), 6.70 (2H, d, J 16.1, 2× CH=), 4.47 (4H, t, J 1.8, 4× Fc-CH), 4.29 (4H, t, J 1.8, 4× Fc-CH), 4.14 (10H, s, 10× Fc-CH), 4.01 (2H, t, J 6.0, CH<sub>2</sub>O), 3.38 (2H, t, J 6.0, CH<sub>2</sub>N<sub>3</sub>) and 1.95–1.75 (4H, m,  $4 \times$  CH<sub>2</sub>);  $\delta_{C}$  (75 MHz, CDCl<sub>3</sub>) 158.0 (C, quat.), 145.5 (C, quat.), 139.2 (C, quat.), 136.8 (C, quat.), 129.2 (CH), 128.1 (CH), 127.2 (CH=), 125.4 (CH=), 125.3 (CH), 113.8 (CH), 83.2 (C, quat.), 81.6 (C, quat.), 69.2 (Fc-CH), 69.1 (Fc-CH), 67.1 (OCH<sub>2</sub>), 66.9 (Fc-CH), 51.2 (N<sub>3</sub>CH<sub>2</sub>), 26.5 (CH<sub>2</sub>) and 25.8 (CH<sub>2</sub>). MS (EI) m/ *z*=793.21 ([M]<sup>+</sup>, 100%). HRMS (ESI): [M]<sup>+</sup>, found 793.20642. C47H43Fe2N3O2 requires 793.20486.

4.2.20. Benzene-1,3,5-tricarboxylic acid tris-(3,5-bis(2-propynyloxy))-ester (10). To a stirred solution of benzylic alcohol  $9^{16}$ (840 mg, 3.8 mmol) and DMAP (732 mg, 6.0 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added 1,3,5-benzenetricarbonyl trichloride<sup>28</sup> (322 mg, 1.2 mmol) under argon and the resulting slurry was stirred at 25 °C for 18 h. The solvent was evaporated, the crude crushed into EtOAc (10 mL) and the insoluble salt was filtered off. Evaporation of solvent yielded the crude product, which was then purified by column chromatography (2% Et<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub>) to give ester 10 as a white solid (720 mg, 78%), mp 117–119 °C; R<sub>f</sub> 0.22 (100% CH<sub>2</sub>Cl<sub>2</sub>);  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 8.91 (3H, s, 3× CH), 6.72 (6H, d, J 2.0, 6× CH), 6.61 (3H, t, J 2.0, 3× CH), 5.36 (6H, s, 3× ArCH<sub>2</sub>O), 4.69 (12H, d, J 2.5,  $6 \times$  CH<sub>2</sub>O) and 2.57 (6H, t, J 2.5Hz,  $6 \times$  CH);  $\delta_{C}$ (75 MHz, CDCl<sub>3</sub>) 164.6 (C, quat.), 158.8 (C, quat.), 137.7 (C, quat.), 134.9 (C, quat.), 131.2 (C, quat.), 107.7 (CH), 102.3 (CH), 78.1 (C, quat.), 76.0 (CH), 67.1 (OCH<sub>2</sub>) and 55.9 (OCH<sub>2</sub>). ESI mass spectrum: calcd for C<sub>48</sub>H<sub>36</sub>NaO<sub>12</sub> [M+Na]<sup>+</sup>: 827.21. Found: 827.19 (100%).

4.2.21. General procedure for the azide-alkyne click reaction catalyzed by Cu(PPh<sub>3</sub>)<sub>3</sub>Br. Dendimer 20. A 10 mL reaction vessel was charged in air with the acetvlene-terminated core **10** (81 mg. 0.1 mmol), the azide 18 (640 mg, 0.80 mmol; 8 equiv), N,N-diisopropylethylamine (60 ul. 0.35 mmol),  $Cu(PPh_3)_3Br^{29}$  (23 mg. 0.025 mmol) and THF (3 mL). The vessel was sealed and submitted to microwave irradiation for 20 min at 140 °C, using an initial power of 70 W. The mixture was then allowed to cool to room temperature, the solvent was evaporated and the product was purified by size exclusion chromatography (100% CH<sub>2</sub>Cl<sub>2</sub>) to give dendrimer 20 as an orange solid (530 mg, 95%);  $\delta_{\rm H}$  (600 MHz, CDCl<sub>3</sub>) 8.88 (3H, s, 3× CH), 7.59 (6H, s, 6× Het–CH), 7.36 (24H, d, J 8.2, 24× Ar–CH), 7.25 (24H, d, / 8.2, 24× Ar–CH), 7.20 (12H, d, / 8.5, 12× Ar–CH), 6.86 (12H, d, J 16.1, 12× CH=), 6.78 (12H, d, J 8.5, 12× Ar–CH), 6.68 (12H, d, J 16.1, 12× CH=), 6.66 (6H, s, 6× Ar–CH), 6.61 (3H, s, 3× Ar–CH), 5.28 (6H, s, 3× CH<sub>2</sub>), 5.11 (12H, s, 6× CH<sub>2</sub>), 4.45 (24H, s, 24× Fc–CH), 4.36 (12H, t, J7.0, 6× CH<sub>2</sub>), 4.28 (24H, s, 24× Fc-CH), 4.13 (60H, s, 60× Fc-CH), 3.91 (12H, t, J 5.9, 6× CH<sub>2</sub>), 3.01 (6H, s, 6× OH), 2.13–1.98 (12H, m,  $6 \times$  CH<sub>2</sub>) and 1.83–1.66 (12H, m,  $6 \times$  CH<sub>2</sub>);  $\delta_{C}$ (75 MHz, CDCl<sub>3</sub>) 164.6 (C, quat.), 159.5 (C, quat.), 157.7 (C, quat.), 145.5 (C, quat.), 143.6 (Het–C, quat.), 139.3 (C, quat.), 137.9 (C, quat.), 136.6 (C, quat.), 134.9 (Ar-CH), 131.1 (C, quat.), 129.2 (Ar-CH), 128.1 (Ar-CH), 127.1 (CH=), 125.5 (CH=), 125.0 (Ar-CH), 122.9 (Het-CH), 113.62 (Ar-CH), 107.5 (Ar-CH), 101.7 (Ar-CH), 83.2 (Fc-C, quat.), 81.4 (C, quat.), 69.2 (Fc-CH), 69.1 (Fc-CH), 66.8 (Fc-CH), 66.7 (ArCH<sub>2</sub>OC(0)+CH<sub>2</sub>OAr), 61.96 (OCH<sub>2</sub>-Het), 50.01 (NCH<sub>2</sub>), 27.1 (CH<sub>2</sub>) and 26.1 (CH<sub>2</sub>). MALDI mass spectrum: calcd for C<sub>330</sub>H<sub>294</sub>Fe<sub>12</sub>N<sub>18</sub>O<sub>24</sub> [M]<sup>+</sup>: 5566.45. Found: 5566.87.

## 4.3. Sample preparation for the pH-dependent absorption measurements

Stock solutions for the dyes (1.0E-5 M to 2.0E-4 M see Table 1 in main text) and TFA in CHCl<sub>3</sub> were prepared. The dye solutions were prepared by mixing 1 or 2 mL of the dye base solution with varying amounts of the TFA solutions and the final volumes adjusted to 5 or 10 mL with CHCl<sub>3</sub>.

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