

Convergent synthesis and light harvesting properties of dendritic boradiazaindacene (BODIPY) appended perylenediimide dyes

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A convergent synthesis methodology, together with “click-chemistry” between azides and terminal alkynes, allows straightforward access to dendritic light harvesting systems. The novel dendrimer reported in this study has eight boradiazaindacene (BODIPY) units at the periphery and a perylenediimide (PDI) dye at the core. We have demonstrated that visible light is effectively collected as a result of the large absorption cross section of the dendrimer and efficiently channeled to the core PDI unit, resulting in a significant antenna effect. While being one of the very few energy transfer systems with a BODIPY and PDI chromophore pair, this novel dendritic molecule is one of the most efficient in light harvesting. The factors that may play important roles as the generation number increases also become apparent when emission characteristics were analyzed in comparison with a lower generation dendrimer.

Introduction

The photosynthetic reaction centre (PRC) is a source of inspiration for many chemists, in terms of efficiency and implementation of light harvesting. Here, a large number of chlorophyll-type and other (carotenoid or tetrapyrrolic) pigment molecules act as antenna and channel the collected photonic energy to a special dimeric arrangement of chlorophyll molecules known as the special pair. This event is mimicked in chemical systems by artificial light harvesting systems. In such systems, organizing a large number of chromophores around an energy acceptor is most effectively realized by a dendritic structure. In recent years, a number of skillfully designed examples of dendritic light harvesting systems (LHS) have appeared in the literature.¹ We are particularly interested in the synthesis of such structures by making use of the “click-chemistry” version² of the well-known Huisgen reaction.

As the donor–acceptor chromophore pair, we prefer boradiazaindacene (BODIPY) and perylenediimide dyes, as we have already demonstrated that very efficient energy transfer is possible within this pair.^{1f} Boradiazaindacenes are well known,³ bright green-emitting fluorescent dyes with many diverse applications, such as fluorescent labeling of biomolecules,⁴ efficient sensitizers for photodynamic therapy,⁵ ion sensing and signaling,⁶ energy transfer cassettes,⁷ light harvesting systems,^{1f,8} and supramolecular polymers.⁹ The parent dye absorbs near 480 nm and emits around 490 nm, but it is

amenable to modifications,^{7c,10} through which the absorption and the emission peaks can be shifted to the red end of the visible spectrum.

Through-space energy transfer efficiency is primarily controlled by two parameters, (1) the distance between the energy donor and acceptor chromophores, and (2) the spectral overlap between the emission spectrum of the energy donor and the absorption spectrum of the energy acceptor. Considering the spectral characteristics of the BODIPY dyes and the bay region-substituted perylenediimide dyes which have typical absorption peaks around 580 nm, we targeted two different dendritic BODIPY-substituted PDI dyes (**7** and **11**). In this design, it is obvious that the peripheral chromophores are to act as antenna with very large cumulative absorption cross sections. In the synthesis scheme shown in Scheme 1, the key intermediates are azidoboradiazaindacene derivative **3**, and the tetra-alkynyl-substituted PDI **6**. The click reactions were carried out in a solvent mixture composed of CHCl₃–EtOH–water. The octaboradiazaindacene-substituted compound **11** was synthesized by making use of a Frechet style convergent approach.¹¹ Thus, the two boradiazaindacene dyes were first tethered to a disubstituted benzylbromide **8**, and then converted to an azide and carried over to the final “click” step, yielding the two dendritic light harvesting molecules.

Results and discussion

In comparing the absorption spectra of compounds **7** and **11** (Fig. 1), it is clear that increasing the number of boradiazaindacene peripheral units from 4 to 8 results in a larger total extinction coefficient at 520 nm. The increase is not exactly 2-fold, but close to 60%. This can be taken as evidence for interchromophoric interactions between the BODIPY units. There is also a small hypsochromic shift (–3 nm) in the absorption spectrum of **11** compared to **7** which may support this conclusion.

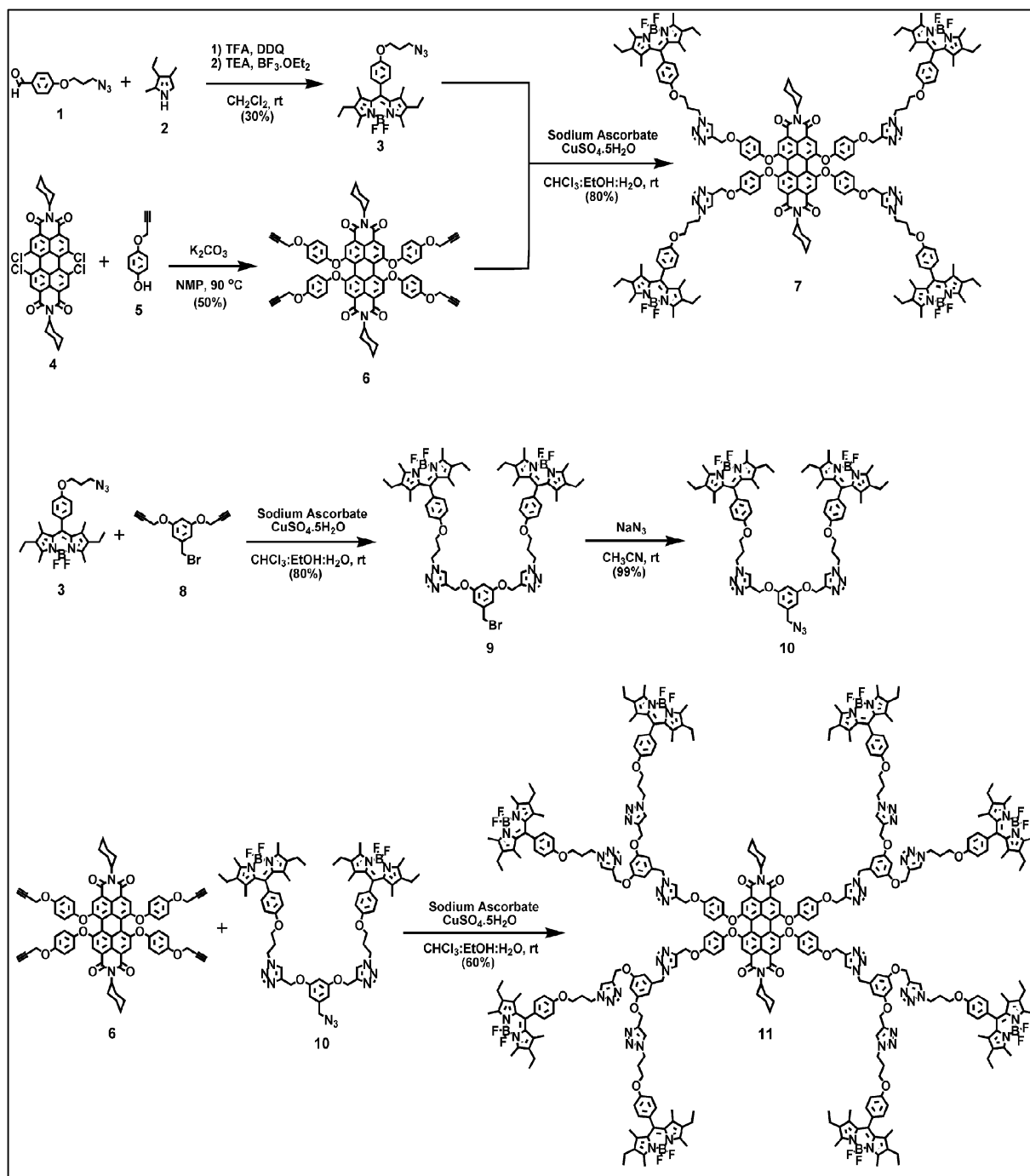
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Scheme 1 Synthesis of the novel light harvesting systems.

The emission spectra (Fig. 2) are more revealing; for an effective comparison, CHCl_3 solutions of equal absorbance at 588 nm (corresponding to the absorption peak of the PDI core) were prepared.

Excitation of a solution of the reference boradiazaindacene **3** at 526 nm (boradiazaindacene absorption peak) yields a very strong emission at around 538 nm. When a solution of the dendrimer **11**, having the same absorption at 526 nm, was excited, very weak emission (almost at the baseline level) from boradiazaindacene chromophores was observed. This is in accordance with the proposed energy transfer scheme.

Time-resolved fluorescence spectroscopy provides solid evidence for the energy transfer: the reference BODIPY dye **3** has an emission lifetime of 4.26 ns (Table 1). The residual emission of the energy donor BODIPY units in compounds **7** and **11** have emission lifetimes of 0.05 and 0.11 ns, respectively, indicating a fast energy transfer. The energy transfer rates (k_{ET}) were calculated for compounds **7** and **11** and the values are 1.77×10^{10} and $6.77 \times 10^9 \text{ s}^{-1}$, respectively.^{8d} Thus, an energy transfer efficiency of 98.7% was calculated for **7**, and 95.7% for the larger dendritic light harvester, **11**.¹² On the other hand, the emission intensity at 615 nm (PDI core emission) is

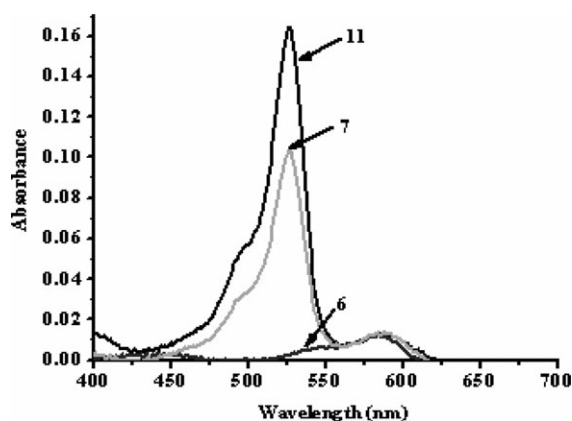


Fig. 1 Absorbance spectra of compounds **6**, **7** and **11** at equal absorbances at 588 nm in CHCl_3 .

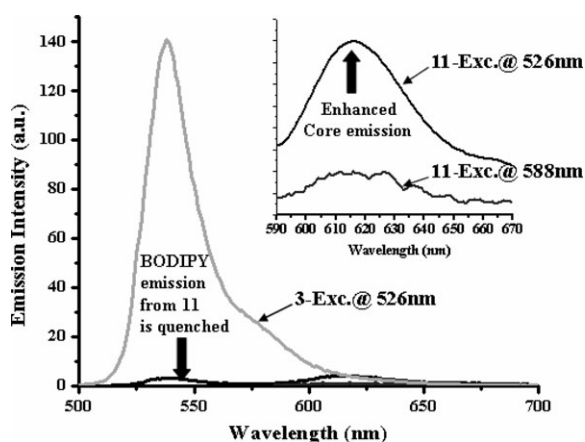


Fig. 2 The emission spectra of **3** and **11** at equal absorbances at 526 nm in CHCl_3 . Inset: enhanced core emission on excitation of the peripheral BODIPY units in the light-harvesting molecule **11**.

enhanced 4-fold when compound **11** is excited at 526 nm as opposed to 590 nm. This is a satisfactory demonstration of the antenna effect. A similar study with compound **7** resulted in a smaller antenna effect, giving a 3.5-fold enhancement.¹⁷ The emissions from the PDI core have comparable lifetimes in the dendritic molecules **7** and **11** and the reference PDI derivative **6**, ranging from 4.95 to 5.57 ns. In compound **11**, the Förster radius (R_0) was calculated as 62 Å, and the average donor–acceptor distance based on the energy-minimized structure of **11** was determined to be 36 Å. This is well within the Förster radius, so efficient energy transfer is to be expected. The differences between compounds **7** and **11** are instructive: in dendritic molecule **7**, the donor and acceptor chromophores are in close proximity, and, as a result, the energy transfer is somewhat more efficient. Not surprisingly, in **11**, some residual BODIPY emission is present. This may be due, at least in part, to the increased distance between the boradiazaindacene and PDI chromophores. One important result is that although the average distance between the antenna chromophores increases on going from **7** to **11**, the efficiency does not decrease significantly and there is a modest increase in the antenna effect.

Table 1 Spectral parameters for the compounds studied: absorption wavelength (λ_{abs}), extinction coefficient (ϵ_{max}), emission wavelength (λ_{ems}), emission lifetime (τ), quantum yield (Φ)^a

| | $\lambda_{\text{abs}}/\text{nm}$ | $\epsilon_{\text{max}}/\text{M}^{-1} \text{ cm}^{-1}$ | $\lambda_{\text{ems}}/\text{nm}$ | τ/ns | $\lambda_{\text{ems}}/\text{nm}$ | τ/ns | Φ^b |
|-----------|----------------------------------|-------------------------------------------------------|----------------------------------|------------------|----------------------------------|------------------|----------|
| 7 | 526 | 240 000 | 540 | 0.05 | 616 | 4.95 | 0.60 |
| | 590 | 45 000 | | | | | |
| 11 | 526 | 408 000 | 540 | 0.11 | 616 | 5.57 | 0.67 |
| | 590 | 45 000 | | | | | |
| 3 | 526 | 62 000 | 540 | 4.26 | | | 0.85 |
| 6 | 590 | 45 700 | | | 616 | 5.40 | 0.27 |

^a Determined in CHCl_3 solution. ^b Rhodamine 6G in ethanol ($\Phi_{\text{r}} = 0.95$) was used as reference.

Conclusions

In building large dendritic systems for efficient light harvesting, inevitably, the distance between the peripheral chromophores and the core increases. While the absorption cross-section increases with increasing generation number, the efficiency of energy transfer tends to decrease. However, with judicious design, if the spectral overlap between the energy donor chromophores and the energy acceptor core is large enough, increased distance can be tolerated. It is clear that BODIPY and tetraaryloxyperilendiimide dyes are a very good match in this regard. Dendritic designs using this pair are very likely to succeed. One can even envision energy cascade systems, where intervening chromophores concentrate and channel the excitation energy to the core chromophore(s). The versatile chemistry of BODIPY is expected to yield such light harvesting systems with highly directional energy transfer. In fact, the earliest examples of such BODIPY-based systems have already appeared in the literature.^{7,8} Their potential in solar light harvesting is also beginning to be appreciated. Our work along these lines is in progress.

Experimental

General

The compounds were characterized and analyzed by nuclear magnetic resonance (NMR) spectroscopy, UV/Vis spectroscopy, and fluorescence spectroscopy. ^1H and ^{13}C NMR spectra of all compounds were recorded in CDCl_3 with a Bruker GmbH DPX-400, 400 MHz high performance digital FT-NMR spectrometer. UV/Vis spectra were recorded with a Varian Bio 100 UV/Vis spectrophotometer. Fluorescence spectra were recorded using a Varian Cary Eclipse fluorescence spectrophotometer. The fluorescence decay measurements were carried out with the TM-3 LaserStrobe time-resolved fluorometer utilizing a pulsed nitrogen/dye laser excitation and the stroboscopic detection system. The dye laser excitation was at 526 and 590 nm. The instrument response function was measured with an aqueous Ludox solution. The decays were analyzed with a multiexponential fitting function by iterative deconvolution and chi-square minimization. Mass spectrometry measurements were done at the Ohio State University Mass Spectrometry and Proteomics Facility, Ohio, USA, or the Kent Mass Spectrometry Laboratory, Kent, UK. All solvents were distilled over CaCl_2 before use. All chemicals were obtained from Aldrich, unless noted otherwise. Merck Silica

Gel 60 F₂₅₄ TLC aluminium sheets were used to monitor reactions by thin layer chromatography. Merck Silica Gel 60 (particle size 0.040–0.0963 mm, 230–400 mesh ASTM) was used in column chromatography.

Syntheses

4-(3-azidopropoxy)benzaldehyde (1). A mixture of 4-(3-bromopropoxy)benzaldehyde (5.37 mmol, 1.3 g) and NaN₃ (13.425 mmol, 0.87 g) in 20 ml DMF was heated at 100 °C overnight. The mixture was poured into water and extracted with CHCl₃ several times. Removal of solvent gave the pure azide compound. Colorless oil (1.05 g, 99%). ¹H NMR (CDCl₃): δ (ppm) 9.85 (s, 1H), 7.81 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 4.17 (t, *J* = 5.8 Hz, 2H), 3.58 (t, *J* = 6.4 Hz, 2H), 2.00–2.15 (m, 2H). ¹³C NMR (CDCl₃): δ (ppm) 190.6, 163.7, 131.9, 130.0, 114.7, 64.9, 48.0, 28.5. Elemental analysis: found C, 59.33; H, 5.49; N, 20.39, C₁₀H₁₁N₃O₂ requires C, 58.53; H, 5.40; N, 20.48.

4,4-difluoro-8-(4-(3-azidopropoxy))phenyl-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4adiazas-indacene (3). 3-Ethyl-2,4-dimethylpyrrole (5.26 mmol, 0.648 g) and compound **1** (2.6 mmol, 0.533 g) were dissolved in 200 ml dry CH₂Cl₂ (argon gas was bubbled through CH₂Cl₂ for 30 min) under argon atmosphere. One drop of TFA was added and the solution stirred at room temperature for 4 h. At this point, a solution of DDQ (2.6 mmol, 0.640 g) in 50.0 ml dry CH₂Cl₂ was added, stirring was continued for 30 min followed by the addition of 3.0 ml Et₃N and 3.0 ml BF₃·OEt₂. After stirring for 30 min, the reaction mixture was washed three times with water and dried over Na₂SO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography (CHCl₃). Orange-red solid (0.374 g, 30%). ¹H NMR (CDCl₃): δ (ppm) 7.10 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 4.05 (t, *J* = 6.4 Hz, 2H), 3.49 (t, *J* = 6.8 Hz, 2H), 2.45 (s, 6H), 2.25 (q, *J* = 7.5 Hz, 4H), 2.01–2.15 (m, 2H), 1.27 (s, 6H), 0.91 (t, *J* = 7.5 Hz, 6H). ¹³C NMR (CDCl₃): δ (ppm) 158.6, 153.1, 139.7, 137.9, 132.2, 130.7, 129.1, 127.7, 114.5, 64.2, 47.8, 28.3, 16.6, 14.1, 12.0, 11.3. Elemental analysis: found C, 65.44; H, 6.91; N, 14.53, C₂₆H₃₂BF₂N₅O requires C, 65.14; H, 6.73; N, 14.61.

***N,N'*-Dicyclohexyl-1,6,7,12-tetra(4-propargyloxyphenoxy) perylene-tetracarboxylic diimide (6).** A mixture of *N,N'*-dicyclohexyl-1,6,7,12-tetrachloro-perylen-3,4,9,10-tetracarboxylic acid diimide **4** (0.72 mmol, 0.500 g), 4-propargyloxyphenol **5** (6.75 mmol, 1.0 g) and K₂CO₃ (7.25 mmol, 1.0 g) in 20 ml NMP was heated at 90 °C overnight. A cooled mixture was poured into 20 ml 10% HCl solution, filtered with suction, and washed three times with water. The resulting precipitate was purified by column chromatography on silica gel (first CHCl₃, then CHCl₃–hexane, (5 : 1)). Red solid (0.410 g, 50%).

¹H NMR (CDCl₃): δ (ppm) 8.01 (s, 4H), 6.85 (s, 16H), 4.86 (m, 2H), 4.63 (s, 8H), 2.55 (s, 4H), 1.01–2.09 (m, 20H). ¹³C NMR (CDCl₃): δ (ppm) 163.7, 156.2, 154.4, 149.4, 132.7, 123.0, 121.1, 119.9, 119.3, 119.1, 116.4, 78.4, 75.7, 56.4, 53.9, 29.1, 26.5, 25.4. Elemental analysis: found C, 75.69; H, 4.68; N, 2.34, C₇₂H₅₄N₂O₂ requires C, 75.91; H, 4.78; N, 2.46. MS (MALDI) 1138.4 (M⁺).

Light harvesting molecule 7

A solution of the compound **3** (0.225 mmol, 0.108 g), compound **6** (0.0535 mmol, 0.061 g), sodium ascorbate (0.0225 mmol, 0.0045 g), and CuSO₄ (0.01125 mmol, 0.0028 g) in a 12 : 1 : 1 mixture of CHCl₃, EtOH and water (14.0 ml) was stirred at room temperature for 72 h. The solvents were removed under reduced pressure and the crude product was purified by column chromatography (CHCl₃). Red solid (0.1309 g, 80%).

¹H NMR (CDCl₃): δ (ppm) 8.00 (s, 4H), 7.65 (s, 4H), 7.12 (d, *J* = 8.4 Hz, 8H), 6.93 (d, *J* = 8.5 Hz, 8H), 6.81 (s, 16H), 5.12 (s, 8H), 4.86–4.95 (m, 2H), 4.65 (t, *J* = 6.6 Hz, 8H), 4.03 (t, *J* = 5.8 Hz, 8H), 2.42 (s, 24H), 2.27 (q, *J* = 7.5 Hz, 16H), 1.00–2.01 (m, 52H), 0.95 (t, *J* = 7.5 Hz, 24H). ¹³C NMR (CDCl₃): δ (ppm) 163.7, 158.9, 156.4, 155.2, 153.6, 149.1, 144.1, 139.9, 138.3, 132.7, 131.1, 129.6, 128.4, 123.1, 122.9, 121.4, 119.8, 119.0, 117.1, 116.1, 114.9, 64.4, 62.6, 47.3, 30.0, 29.1, 26.5, 21.8, 17.0, 14.5, 12.4, 11.8. MS (MALDI) *m/z* = 3036.4 (M – F)⁺.

Compound 9

A solution of the compound **3** (0.626 mmol, 0.300 g), compound **8** (0.313 mmol, 0.0873 g), sodium ascorbate (0.0626 mmol, 0.0124 g), and CuSO₄ (0.0313 mmol, 0.0078 g) in a 12 : 1 : 1 mixture of CHCl₃, EtOH and water (42.0 ml) was stirred at room temperature for 72 h. The solvents were removed under reduced pressure and the crude product was purified by column chromatography (3% CHCl₃–MeOH). Orange-red solid (0.155 g, 40%).

¹H NMR (CDCl₃): δ (ppm) 7.56 (s, 2H), 7.11 (d, *J* = 8.5 Hz, 4H), 6.92 (d, *J* = 8.4 Hz, 4H), 6.56 (s, 2H), 6.49 (s, 1H), 5.08 (s, 4H), 4.62 (t, *J* = 6.2 Hz, 4H), 4.35 (s, 2H), 4.02 (t, *J* = 4.0 Hz, 4H), 2.44 (s, 12H), 2.37 (p, *J* = 7.4 Hz, 4H), 2.22 (q, *J* = 7.5 Hz, 8H), 1.24 (s, 12H), 0.95 (t, *J* = 7.5 Hz, 12H). ¹³C NMR (CDCl₃): δ (ppm) 159.5, 158.8, 153.6, 143.7, 140.0, 138.3, 132.7, 131.1, 129.6, 128.4, 123.1, 114.9, 108.4, 102.1, 64.3, 62.1, 47.2, 33.2, 29.9, 17.0, 14.5, 12.4, 11.8.

Precursor 10

A mixture of compound **9** (0.121 mmol, 0.150 g) and NaN₃ (0.15 mmol, 0.0097 g) in 20.0 ml CH₃CN was stirred at room temperature overnight. The mixture was extracted with chloroform three times. Removal of solvent gave the pure azide compound.

¹H NMR (CDCl₃): δ (ppm) 7.56 (s, 2H), 7.11 (d, *J* = 8.3 Hz, 4H), 6.92 (d, *J* = 7.8 Hz, 4H), 6.54 (s, 1H), 6.49 (s, 2H), 5.10 (s, 4H), 4.55 (t, *J* = 6.6 Hz, 4H), 4.17 (s, 2H), 3.97 (t, *J* = 6.8 Hz, 4H), 2.44 (s, 12H), 2.37 (p, *J* = 7.4 Hz, 4H), 2.22 (q, *J* = 7.5 Hz, 8H), 1.24 (s, 12H), 0.95 (t, 12H). ¹³C NMR (CDCl₃): δ (ppm) 159.7, 158.9, 153.5, 143.7, 140.0, 138.3, 132.7, 131.1, 129.6, 128.4, 123.2, 114.9, 107.4, 101.7, 64.3, 62.1, 54.6, 47.2, 29.6, 17.0, 14.5, 12.4, 11.8.

Dendrimer 11

A solution of the compound **6** (0.0263 mmol, 0.030 g), compound **10** (0.105 mmol, 0.1232 g), sodium ascorbate (0.0105 mmol, 0.0021 g), and CuSO₄ (0.00525 mmol, 0.0013 g) in a 12 : 1 : 1 mixture of CHCl₃, EtOH and water (28.0 ml) was

stirred at room temperature for 72 h. The solvents were removed under reduced pressure and the crude product was purified by column chromatography (3% CHCl₃–MeOH). Red solid (0.0937 g, 60%). ¹H NMR (CDCl₃): δ (ppm) 8.00 (s, 4H), 7.64 (s, 12H), 7.12 (d, *J* = 8.3 Hz, 16H), 6.92 (d, *J* = 8.5 Hz, 16H), 6.82 (s, 16H), 6.54 (s, 1H), 6.47 (s, 2H), 5.38 (s, 8H), 5.06 (s, 24H), 4.65 (t, *J* = 6.4 Hz, 16H), 4.02 (t, *J* = 6.6 Hz, 16H), 2.42 (s, 48H), 2.37 (p, *J* = 7.4 Hz, 16H), 2.22 (q, *J* = 7.4 Hz, 32H), 1.24 (s, 48H), 0.91 (t, *J* = 7.5 Hz, 48H). MS (MALDI) *m/z* = 6039.5 (*M* – *F* + 3*K*)⁺.

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