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Dendron-decorated cyanine dyes for optical limiting applications in the range of telecommunication wavelengths

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Cyanine dyes decorated with 2,2-bis(methylol)propionic acid (bis-MPA) based dendrons up to third generation were synthesized. Dendrons were attached to the chromophore using a "click chemistry" reaction. Photophysical characterizations of these dyes show intense absorption and emission in the near-infrared (NIR), while nonlinear transmission experiments of the dendron-decorated chromophores indicate that properties in the IR of the parent dyes are conserved. This synthetic approach is a crucial preliminary step towards the preparation of solid functional materials for optical limiting (OL) applications in the IR.

With the development of laser based technologies, there is an increasing need for devices able to protect detectors against intense illumination. In this context, optical limiting (OL) based on multiphotonic absorption of organic compounds has been widely applied to perform protection in the visible and NIR spectral range [400–1000 nm][1] and has been recently extended to up to telecommunication wavelengths [1300–1600 nm].[2] For such an application, chromophores featuring (i) a strong two-photon absorption (TPA) and excited state absorption (ESA) properties, as well as (ii) high solubility in organic solvents (around 100 g L^{-1}) are required. This latter requirement is certainly the reason why only a few papers have reported real optical limiting experiments in the IR, while numerous dipolar,[3] quadrupolar[4] porphyrin or coordination complex[5] based-chromophores have been described for TPA application in this spectral range. Furthermore, it is important to design chromophores that are able to avoid aggregation phenomenon in highly concentrated solution and particularly in the solid state when doped in polymer or sol–gel matrix, which represents the ultimate steps toward the design of a real device. In order to tackle the aggregation problem, some of us decorated the chromophores with dendrons.[6] The steric hindrance afforded by these bulky substituents is known to enhance the solubility and prevent aggregation and quenching of the excited states. In this context, stable and transparent dendrons based on 2,2-bis(methylol)propionic acid (bis-MPA) are very attractive for photonic applications. This strategy has been successfully applied to porphyrins, polythiophenes and platinum acetylides.[6] In the meantime, "click chemistry" and especially the copper-catalyzed 1,3-dipolar cycloaddition between alkynes and azides (CuAAC) has gained growing interest in the field of dendrimers synthesis and more generally in the field of materials science.[7]

In this Letter, we present the synthesis of functionalized cyanine dyes[2a] decorated with bis-MPA based dendrons linked to the chromophore through a "click chemistry" reaction. Their photophysical and nonlinear optical limiting properties are described and compared to that of the parent cyanine dye.

The starting material for these syntheses is the chloroheptamethine **Cy-1** (Scheme 1). The synthesis and optical properties of this dye have already been reported.[2a] For this class of compound, substitution of the *meso*-chlorine atom is a powerful way to introduce various functional moieties.[8] Following this strategy, **Cy-2** featuring a *meso*-phenolate group was synthesized by the reaction of **Cy-1** with a solution of sodium hydride and phenol in DMF at room temperature (RT) (Scheme 1) and recovered with a 63% yield after precipitation in *n*-pentane. This chromophore will be used as a reference in order to compare the optical activity of the dendronized molecules. The same reaction, carried out with hydroxybenzyl alcohol, led to the formation of **Cy-3** (72% yield)—an hydroxyl-functionalized cyanine that will be used as the starting material for the preparation of dendronized chromophores. It is worth noting that no protection of the hydroxybenzyl moieties is required, which makes the functionalization of the cyanine dye easier. In our hands, further esterification between **Cy-3** and dendrons possessing a carboxylic acid at the focal point has been found to be incomplete with residual by-products difficult to separate, and consequently this first functionalization procedure has been discarded.[9] Therefore, a new synthetic approach involving "click chemistry" has been attempted. In order to introduce the azide end-group precursor to "click chemistry" reactions, **Cy-3** was reacted with anhydride **A**[10] and DMAP in dichloromethane (DCM) giving **Cy-4**. This latter compound was further reacted with an excess of a polyester dendrons of second (resp. third) generation possessing an alkyne at the focal point **D2** (resp. **D3**) in THF–water in the presence of copper iodide and sodium ascorbate as the catalytic system (Scheme 1). This method allowed the preparation of **Cy-5** and **Cy-6** in acceptable (53% and 35%) yield, respectively. The removal of the excess alkyne and of the catalysts was carried out by filtration over silica and recrystallization from diethyl

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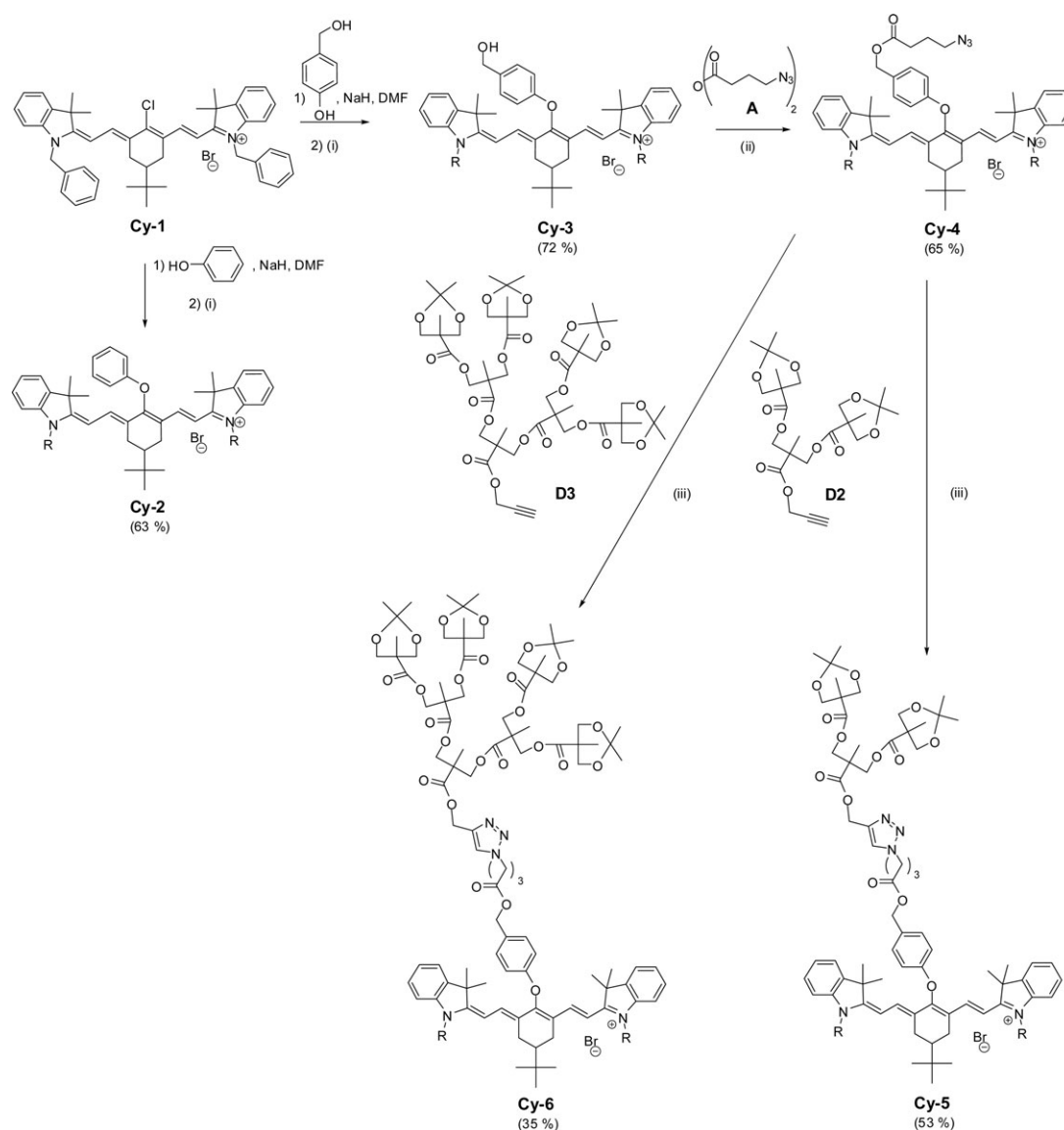
Scheme 1 Reagent and conditions: (i) DMF, RT, 6 h, (ii) DMAP, DCM, RT, 12 h (65%), (iii) $CuSO_4$, sodium ascorbate, THF–water, 50 °C, 48 h.

ether. The purity of the product was confirmed by ^{1}H NMR spectroscopy and MALDI-TOF spectrometry (Fig. 1). This
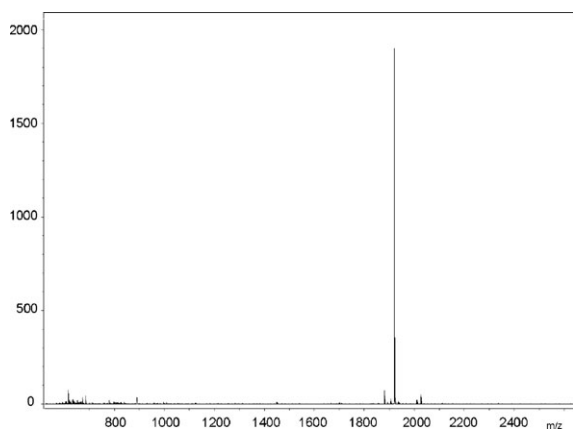

Fig. 1 MALDI-TOF spectrum of **Cy-6**.

convergent synthesis allows the easy synthesis of the monodisperse dendronized chromophore and seems to be extendable to the synthesis of dendronized chromophores of higher generations.

All the compounds present the characteristic absorption spectra of cyanine dyes (Table 1) with an intense NIR absorption (for example, λ_{max}(**Cy-6**) = 778 nm and ε = 170 000 L mol^{-1} cm^{-1}) and a shoulder at higher energy (Fig. 2). Both dendron-decorated and reference **Cy-2** dyes present exactly the same maximal absorption wavelength (λ_{max} = 778 nm) with similar extinction coefficients. They also feature the characteristic emission properties (Table 1) of the cyanine compounds with emission maxima in the NIR (for example, λ_{em}(**Cy-6**) = 800 nm, Fig. 2). As expected, the maximal absorption and emission wavelengths of **Cy-2–6** are slightly blue-shifted compared to the parent chloro-heptamethine **Cy-1**.[8a] All these photophysical data show that the typical linear optical properties of the cyanines are conserved for the dendron-decorated dyes.
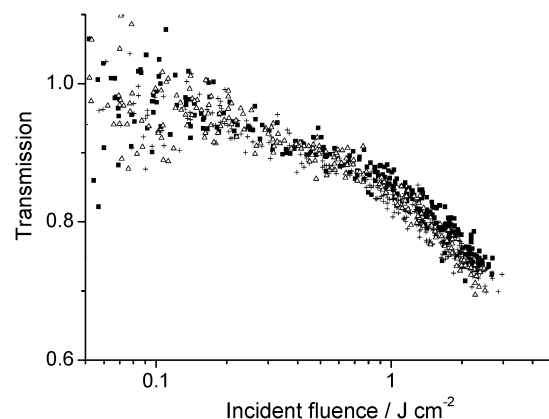
Table 1 Photophysical data in dichloromethane solution

Compound	λ_{max}/nm	ε_{max}/L mol^{-1} cm^{-1}	λ_{em}/nm	$Th_{OL}{}^a$/J cm^{-2}	$T_{min}{}^b$ (%)
Cy-1[c]	794	350 000	817	0.4 ± 0.2	70 ± 5
Cy-2	778	190 000	802	0.4 ± 0.2	70 ± 5
Cy-5	778	210 000	803	0.4 ± 0.2	70 ± 5
Cy-6	778	170 000	800	—	—

[a] Th_{OL} is the OL threshold; this value is graphically determined as the intersection between the linear and the nonlinear part of the OL curve. [b] T_{min} is the transmission reached for the maximal intensity of the laser (2.5 J cm^{-2}). [c] see ref. 2a.
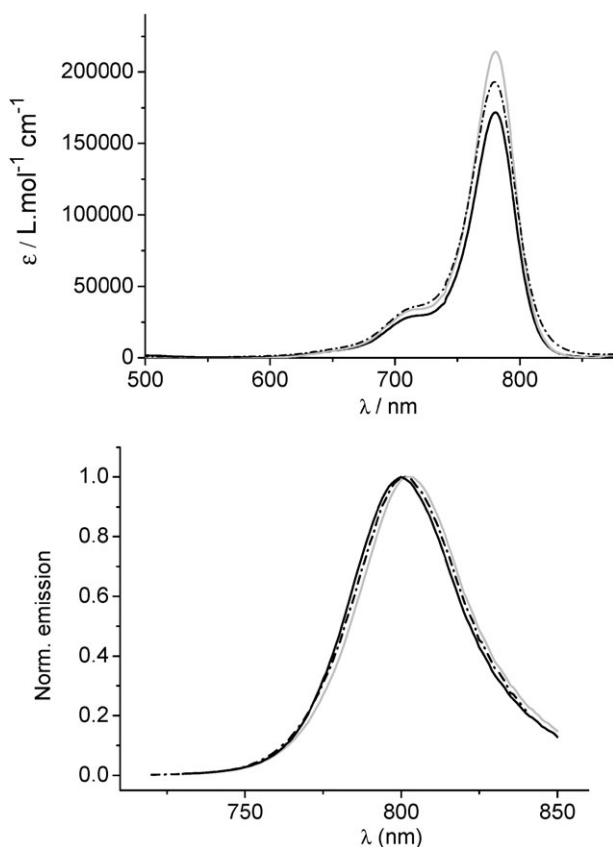
Fig. 2 Absorption (top) and normalized emission (bottom) spectra of **Cy-2** (dash line), **Cy-5** (grey) and **Cy-6** (black) in DCM at room temperature.

Fig. 3 Nonlinear transmission curves at 1420 nm in DCM solution of **Cy-1** (△),**Cy-2** (+) and **Cy-5** (■) ($c = 0.1$ mol L^{-1})

In order to explore the NLO properties of these dyes, nonlinear transmission experiments were also carried out. It is worth noting that these NLO experiments require very high solubility of the dyes. The dendron-decorated dye **Cy-5** presents the typical behavior of optical limiters (Fig. 3): for the operating wavelength, the highly concentrated solution (0.1 mol L^{-1} in dichloromethane) is transparent at low laser intensity and a decrease of the transmission (T) is observed at higher energy. The OL threshold Th_{OL} appeared for an incident fluence of around 0.4 J cm^{-2} and the transmission T_{min} reached for the maximal input energy is 70% (Fig. 3 and Table 1). The relative dispersity of the experimental data allow the graphical determination of Th_{OL} to be given with a precision of around 50%.[2a] It is worth noting that, in this experiment, the minimal transmission value T_{min} is limited by the power of the laser and not by the NLO activity of the

chromophores. Fig. 3 also shows that at this wavelength, the dendronized chomophore **Cy-5** and the reference **Cy-2** possess the same OL threshold ($Th_{OL} = 0.4$ J cm^{-2}) and the same minimal transmission ($T_{min} = 70\%$). These results mean that the presence of the dendrons do not affect the NLO properties of the chromophore. For these solutions, the two-photon induced ESA is believed to be the OL mechanism, as already observed for similar cyanine dyes.[2a] It is also interesting to note that comparable OL data are also obtained for the parent dye **Cy-1** (Fig. 3).[2a] This experiment illustrate that the modification on the *meso*-position of the chloroheptamethine is an efficient strategy to introduce isolating functionalities on the molecule, keeping its NLO properties.

In conclusion, chromophores featuring different end-groups (hydroxy, azide) linked to the *meso*-position of heptamethine cyanine have been synthesized and bis-MPA based dendrons have been linked to the chromophore using "click chemistry". The general synthetic procedure seems to be suitable for the synthesis of chromophores bearing higher generation dendrons. The linear and nonlinear optical studies validate this dendron strategy for cyanine based optical limiters. Indeed, these dendron-decorated chromophores present similar absorption and optical limiting properties as the parent dyes. These NLO-active chromophores, by the introduction of isolating sites minimizing aggregation and chromophore interactions, open interesting possibilities for the design of materials for solid state OL purposes.

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Experimental

General

All reactions were routinely performed under argon. NMR spectra (^{1}H, ^{13}C) were recorded at room temperature on a BRUKER AC 200 operating at 200.13 MHz and 50.32 for ^{1}H and ^{13}C, respectively and on a VARIAN Unity Plus operating at 499.84 MHz for ^{1}H NMR for variable-temperature experiments. Data are listed in parts per million (ppm) and are reported relative to tetramethylsilane (^{1}H, ^{13}C), residual solvent peaks being used as internal standard (CHCl$_3$ ^{1}H: 7.26 ppm, ^{13}C: 77.36 ppm). UV-visible spectra were recorded on a Jasco V-550 spectrophotometer in diluted dichloromethane solution (ca. 10^{-5} mol L^{-1}). The luminescence spectra were measured using a Horiba–Jobin–Yvon Fluorolog-3® spectrofluorimeter, equipped with a three-slit double-grating excitation and emission monochromator with dispersions of 2.1 nm mm^{-1} (1200 grooves mm^{-1}). Nonlinear transmission experiments were carried out with 1420 nm as incident wavelength using a ns-optical parametric oscillator pumped by a frequency tripled Nd:YAG laser source; the complete experimental set-up is described elsewhere.[2a] High resolution mass spectrometry measurements and elemental analysis were performed at the Service Central d'Analyse du CNRS (Vernaison, France). Column chromatography was performed on Merck Gerduran 60 (40–63 μm) silica. Compound **Cy-1** was prepared according to a published procedure.[2a]

Syntheses

Cy-2. Phenol (40 mg, 0.43 mmol, 1.1 equiv.) was dissolved in freshly distilled DMF (10 mL) under argon. NaH (19 mg, 1.2 equiv.) was added. The mixture was stirred at RT for 30 min and was added dropwise to a solution of **Cy-1** (300 mg, 0.39 mmol, 1 equiv.) dissolved in DMF (10 mL). The solution was stirred at RT for 8 h, then quenched with slow addition of aqueous diluted solution of hydrochloric acid and DCM (50 mL). The organic layer was washed with water (3 × 25 mL), brine (25 mL), dried with sodium sulfate and the solvents were evaporated. The crude mixture was dissolved in the minimum amount of DCM and precipitated in pentane to afford a green solid (180 mg, 56%.). ^{1}H NMR (200.13 MHz, CDCl$_3$): δ 0.99 (9H, s), 1.31 (6H, s), 1.35 (s, 6H), 2.06 (dd, ^3J = 13 Hz, ^2J = 13 Hz, 2H), 2.60 (dd, ^3J = 2 Hz, ^2J = 13 Hz, 2H), 5.32 (4H, s), 6.00 (d, ^3J = 14 Hz, 2H), 7.2–7.5 (m, 23H), 7.80 (d, ^3J = 14 Hz, 2H).^{13}C NMR (50.32 MHz, CDCl$_3$): δ 25.3, 27.5, 27.8, 27.9, 32.5, 42.6, 48.2, 48.9, 100.9, 110.9, 114.6, 122.2, 122.7, 123.3, 125.2, 126.7, 128.3, 128.9, 129.3,130.4, 134.4, 140.8, 142.1, 142.7, 159.6, 164.2, 172.1. MS (ESI+): MH$^+$ = 749.4462 (calc. for C$_{46}$H$_{51}$N$_5$O: 649.4471). Anal. calcd for: C$_{54}$H$_{57}$N$_2$O: C, 78.15, H, 6.92, N, 3.38, Found: C, 78.24, H, 7.02, N, 3.37%.

Cy-3. Synthesis was carried out using the same procedure as for **Cy-2** but using 4-hydroxybenzyl alcohol instead of phenol leading to the formation of a green solid (810 mg, 72%). ^{1}H NMR (200.13 MHz, CDCl$_3$): δ 0.98 (s, 9H), 1.28 (m, 1H), 1.32 (s, 6H), 1.37 (s, 6H), 2.0–2.1 (m, 2H), 2.59 (dd, ^3J = 2 Hz, ^2J = 13 Hz, 2H), 4.65 (s, 2H), 5.21 (m, 4H), 5.89 (d, ^3J = 14 Hz, 2H), 6.87 (d, ^3J = 8 Hz, 1H), 7.0–7.4 (m, 18H), 7.45

(d, ^3J = 8 Hz, 2H), 7.85 (d, ^3J = 14 Hz, 2H). ^{13}C NMR (50.32 MHz, CDCl$_3$): δ 25.3, 27.5, 27.9, 28.1, 32.5, 42.6, 48.2, 49.2, 63.6, 100.4, 110.6, 114,3, 122.5, 123.1, 125.3, 126.5, 128.4, 128.8, 129.3, 129.4, 134.1, 137.2, 140.9, 142.6, 158.7, 165.3, 172.4. MS (ES): M$^+$ = 779.5 (calcd for C$_{55}$H$_{59}$N$_2$O$_2$: 779.5). Anal. calc. for: C$_{45}$H$_{59}$N$_2$O$_2$Br: C, 76.82, H, 6.92, N, 3.26, Found: C, 76.30, H, 7.08, N, 2.96%.

Cy-4. Compound **Cy-3** (210 mg, 0.24 mmol, 1 equiv.), 3-azidopropanoic anhydride (117 mg, 2 equiv.) and DMAP (60 mg, 2 equiv.) were dissolved in DCM (5 mL). The solution was stirred at room temperature overnight. Water (5 mL) was then added, and the solution was stirred for 3 h. The layers were separated and the organic layer was extracted with aqueous Na$_2$CO$_3$ 10% (3 × 20 mL) then with a diluted solution of aqueous hydrochloric acid (20 mL). The solution was dried over magnesium sulfate and the solvents were evaporated. The crude product was precipitated in a DCM–diethyl ether solution to afford a green solid (150 mg, 64%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.98 (s, 9H), 1.28 (m, 1H), 1.34 (s, 6H), 1.46 (s, 6H), 1.82 (q, ^3J = 7 Hz, 2H), 2.0–2.1 (m, 2H), 2.35 (t, ^2J = 7 Hz, 2H) 2.59 (dd, ^3J = 2 Hz, ^2J = 13 Hz, 2H), 3.26 (t, ^3J = 7 Hz, 2H), 5.01 (s, 2H), 5.29 (m, 4H), 5.96 (d, ^3J = 14 Hz, 2H), 6.91 (d, ^3J = 8 Hz, 2H), 7.0–7.4 (m, 20H), 7.75 (d, ^3J = 14 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 24.0, 25.1, 27.3, 27.7, 27.8, 30.9, 32.3, 42.4, 48.1, 48.8, 50.4, 51.6, 65.6, 100.8, 110.8, 114.7, 122.1, 122.8, 125.1, 126.5, 128.2, 128.8, 129.2, 130.0, 130.5, 134.1, 140.6, 141.7, 142.5, 159.3, 163.8, 171.9, 172.3. MS (MALDI-TOF): M$^+$ = 890.485 (calc. for C$_{59}$H$_{64}$N$_5$O$_3$: 890.500).

Cy-5. (General procedure for triazole synthesis). Compound **Cy-4** (180 mg, 0.19 mmol, 1 equiv.) and the dendron **D2** (103 mg, 1.1 equiv.) were dissolved in THF (10 mL). Sodium ascorbate (115 mg, 3 equiv.), copper sulfate (145 mg, 3 equiv.) and 5 drops of water were then added. The solution was stirred 48 h at 50 °C. The solution was the filtrated through a silica plug (washed with DCM–methanol 9 : 1) and the solvents were evaporated. The crude was dissolved in DCM (20 mL), and the organic layer was extracted with diluted aqueous Na$_2$CO$_3$ (20 mL), water, and 10% HCl. After evaporation of the solvents, the product was precipitated in DCM–diethyl ether to afford a green solid (140 mg, 53%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.94 (s, 9H), 1.01 (s, 12H), 1.19 (s, 6H), 1.24 (s, 3H) 1.30 (s, 6H), 1,32 (s, 6H), 1.9–2.1 (m, 4H), 2.30 (t, ^2J = 7 Hz, 2H), 2.66 (dd, ^3J = 2 Hz, ^2J = 13 Hz, 2H), 3.55 (d, ^3J = 11 Hz, 4H), 3.91 (d, ^3J = 11 Hz, 4H), 4.1–4.2 (m, 4H), 4.30 (t, ^3J = 7 Hz, 2H), 4.99 (s, 2H), 5.12 (s, 2H), 5.35 (d, J = 2 Hz, 2H), 5.48 (d, J = 12 Hz, 2H), 6.19 (d, J = 14 Hz, 2H), 7.2–7.7 (m, 22H), 7.73 (d, ^3J = 14 Hz, 2H), 8.06 (s, 1H). MS (MALDI-TOF): M$^+$ = 1374.752 (calc. for C$_{59}$H$_{64}$N$_5$O$_3$: 1374.731).

Cy-6. The product was synthesized according to the general procedure for triazole synthesis from **Cy-4** and the dendron **D3** in 35% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.97 (s, 9H), 1–1.4 (m, 54H), 1.9–2.1 (m, 4H), 2.30 (t, ^2J = 7 Hz, 2H), 2.66 (dd, ^3J = 2 Hz, ^2J = 13 Hz, 2H), 3.55 (d, ^3J = 11 Hz, 8H), 3.96 (d, ^3J = 11 Hz, 8H), 4.1–4.2 (m, 12H), 4.32 (t, ^3J = 7 Hz, 2H), 5.01 (s, 2H). 5.14 (s, 2H), 5.38 (d, J = 2 Hz,

2H), 5.51 (d, J = 12 Hz, 2H). 6.22 (d, ^3J = 14 Hz, 2H), 7.11 (d, ^3J = 8 Hz, 2H), 7.2–7.7 (m, 20H), 7.75 (d, ^3J = 14 Hz, 2H), 8.10 (s, 1H). MS (MALDI-TOF): M^+ = 1918.987 (calc. for $C_{59}H_{64}N_5O_3$: 1918.983).

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