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► **To cite this version:**

Pierre-Antoine Bouit, Robert Westlund, Patrick Feneyrou, Olivier Maury, Michael Malkoch, et al.. Dendron-decorated cyanine dyes for optical limiting applications in the range of telecommunication wavelengths. *New Journal of Chemistry*, 2009, 33 (5), pp.964-968. 10.1039/B822485D . hal-01320593

HAL Id: hal-01320593

<https://hal.science/hal-01320593>

Submitted on 27 Nov 2019

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Dendron decorated cyanine dyes for optical limiting applications at telecommunication wavelengths.

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Abstract—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 “click chemistry” reaction. Photophysical characterizations of these dyes show intense absorption and emission in the near-infrared (NIR) and nonlinear transmission experiments of the dendron-decorated chromophores indicate that the nonlinear optical (NLO) properties of the parent dyes are conserved. Finally, this synthetic approach is an interesting way to prepare functional materials for optical limiting (OL) applications

Introduction.

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 recently extended to up to telecommunications wavelengths [1300 - 1600 nm].² For such application are required chromophores featuring (i) 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) limiting aggregation phenomenon in highly concentrated solution or in polymer matrix. This latter requirement is certainly the reason why only few papers reported real optical limiting experiment in the NIR while numerous dipolar,³ quadrupolar⁴ porphyrine or coordination complexes⁵ based-chromophores were described for TPA application in this spectral range. In order to tackle the aggregation problem, some of us decorated the chromophores with dendrons in order to enhance the solubility, prevent aggregation and quenching of the excited states. Indeed, dendrons based on 2,2-bis(methylol)propionic acid (bis-MPA) are stable and transparent which make them attractive for photonic applications. This strategy has been successfully applied to porphyrines, 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 paper, we present the synthesis of functionalized cyanines dyes^{2a} decorated with bis-MPA based dendrons linked to the chromophore through “click chemistry” reaction. Their photophysical and nonlinear optical limiting properties were described and compared to that of the parent cyanine dye.

Results and discussion.

The starting material for these syntheses is the chloro-heptamethine **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 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 starting material for the preparation of dendronized chromophores. It is worth noting that no protection of the hydroxybenzyl moieties is required which make the functionalization of the cyanine dye easier. In our hand, further esterification between **Cy-3** and dendrons possessing a carboxylic acid at the focal point have been found to be incomplete with residual by-products difficult to separate, and consequently this first functionalization procedure have been discarded.⁹ Therefore, a new synthetic approach involving “click chemistry” has been attempted.^{1d} In order to introduce the azide end-group precursor to “click chemistry” reactions, **Cy-3** was reacted with the 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**¹¹ in THF-water in the presence of copper iodide and sodium ascorbate as catalytic system (Scheme 1). This method allowed the preparation of **Cy-5** and **Cy-6** in acceptable 53 % and 35% yield respectively. The removing of the excess of alkyne and of the catalysts was made by filtration over silica and recrystallization from diethyl ether. The purity of the product was checked by ¹H NMR spectroscopy and MALDI-TOF spectrometry (Figure 1). This convergent synthesis

allows the easy synthesis of monodisperse dendronized chromophore and seems to be generalizable to the synthesis of dendronized chromophores of higher generation.

All the compounds present the characteristic absorption spectra of cyanine dyes (Table 1) with an intense NIR absorption (for example $\lambda_{\max}(\mathbf{Cy-6}) = 778 \text{ nm}$ and $\epsilon = 170000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) and a shoulder at higher energy (Figure 2). Both dendron decorated and reference **Cy-2** dyes present exactly the same maximal absorption wavelength ($\lambda_{\max} = 778 \text{ nm}$) 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 $\lambda_{\text{em}}(\mathbf{Cy-6}) = 800 \text{ nm}$, Figure 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.

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. 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; complete experimental set-up is described elsewhere.^{2a} The dendron decorated dye **Cy-5** present the typical behavior of optical limiters (Figure 3, red curve): for the operating wavelength, the highly concentrated solution ($0.1 \text{ mol}\cdot\text{L}^{-1}$ in dichloromethane) is transparent at low laser intensity and a decrease of the transmission (T) is observed at higher energy. The OL threshold T_h appeared for an incident fluence of around $0.4 \text{ J}\cdot\text{cm}^{-2}$ and the transmission T_{\min} reached for the maximal input energy is 70 % (Figure 3 and Table 1). The relative dispersity of the experimental data make that the graphical determination of T_h is given with a precision of around 50%.^{2a} In addition, 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. Figure 3 also

shows that at this wavelength, the dendronized chromophore **Cy-5** and the reference **Cy-2** possess the same OL threshold ($Th = 0.4 \text{ J.cm}^{-2}$) 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 the same OL data are also obtained for the parent dye **Cy-1** (figure 3, black curve).^{2a} Changing the *meso*-chlorine atom of an heptamethine dye by an oxygen atom does not affect significantly its NLO properties. This experiment illustrates that the modification on the *meso*-position of the chloro-heptamethine is an efficient strategy to introduce functionalities on the molecule while keeping intact its optical properties.

Concluding remarks

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”. All the results obtained during the linear and nonlinear optical studies validate the dendron strategy for cyanine based optical limiter. Indeed, the dendron decorated chromophores present the same absorption and optical limiting properties than the parent dyes. The general synthetic procedure seems to be suitable for the synthesis of chromophores bearing higher generation dendrons. It may be also interesting to introduce additional end-groups for further grafting into solid matrix. Finally, these NLO-active chromophores open interesting perspectives for the design of materials for solid state OL purpose.

Experimental section

General. All reactions were routinely performed under argon. NMR spectra (^1H , ^{13}C) were recorded at room temperature on a BRUKER AC 200 operating at 200.13 MHz and 50.32 for ^1H and ^{13}C respectively and on a VARIAN Unity Plus operating at 499.84 MHz for ^1H NMR for variable temperature experiments. Data are listed in parts per million (ppm) and are reported relative to tetramethylsilane (^1H , ^{13}C), residual solvent peaks being used as internal standard (CHCl_3 ^1H : 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 $^{-1}$). 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 published procedure.^{2a}

Cy-2. Phenol (40 mg, 0.43 mmol, 1.1 eq.) was dissolved in freshly distilled DMF (10 mL) under argon. NaH (19 mg, 1.2 eq.) 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 eq.) 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 x 25 mL), brine (25 mL), dried with sodium sulfate and the solvents were evaporated. The crude was dissolved in the minimum amount of DCM and precipitated in pentane to afford a green solid (180 mg, 56 %). ^1H 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+): $MH^+ = 749.4462$ (calcd for $C_{46}H_{51}N_5O$: 649.4471). Anal. calcd for: $C_{54}H_{57}N_2O$: 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 than **Cy-2** using 4-hydroxybenzyl alcohol instead of phenol leading to the formation of a green solid (810 mg, 72 %). 1H 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 $C_{55}H_{59}N_2O_2$: 779.5). Anal. calcd for: $C_{45}H_{59}N_2O_2Br$: 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 eq.), 3-azidopropanoic anhydride (117 mg, 2 eq.) and DMAP (60 mg, 2 eq.) are dissolved in DCM (5 mL). The solution is stirred at room temperature overnight. Water (5 mL) is then added, and the solution is stirred for 3 h. The layers are separated and the organic layer is extracted with aqueous Na_2CO_3 10% (3 x 20 mL) then with a diluted solution of aqueous hydrochloric acid (20 mL). The solution is dried over magnesium sulfate and the solvents are evaporated. The crude product is precipitated in a DCM-diethyl ether solution to afford a green solid (150 mg, 64%). 1H 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): $M^+ = 890,485$ (calcd for $C_{59}H_{64}N_5O_3$: 890.500).

Cy-5. (general procedure for triazole synthesis) Compound **Cy-4** (180 mg, 0.19 mmol, 1 eq.) and the dendron **D2** (103 mg, 1.1 eq.) are dissolved in THF (10 mL). Sodium ascorbate (115 mg, 3 eq.), copper sulfate (145 mg, 3 eq.) and 5 drops of water are then added. The solution is stirred 48 h at 50°C. The solution is filtered through a silica plug (washed with DCM-Methanol 9-1) and the solvents are evaporated. The crude is dissolved in DCM (20 mL), and the organic layer is extracted with diluted aqueous Na₂CO₃ (20 mL), water, and 10% HCl. After evaporation of the solvents, the product is precipitated in DCM-diethyl ether to afford a green solid (140 mg, 53%). ¹H 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, ²*J* = 7 Hz, 2H), 2.66 (dd, ³*J* = 2 Hz, ²*J* = 13 Hz, 2H), 3.55 (d, ³*J* = 11 Hz, 4H), 3.91 (d, ³*J* = 11 Hz, 4H), 4.1- 4.2 (m, 4H), 4.30 (t, ³*J* = 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, ³*J* = 14 Hz, 2H), 7.2-7.7 (m, 22H), 7.73 (d, ³*J* = 14 Hz, 2H), 8.06 (s, 1H). MS (MALDI-TOF): M⁺ = 1374.752 (calcd for C₅₉H₆₄N₅O₃: 1374.731).

Cy-6. The product was synthesized according the general procedure for triazole synthesis from **Cy-4** and the dendron **D3** with a 35% yield. ¹H 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, ²*J* = 7 Hz, 2H), 2.66 (dd, ³*J* = 2 Hz, ²*J* = 13 Hz, 2H), 3.55 (d, ³*J* = 11 Hz, 8H), 3.96 (d, ³*J* = 11 Hz, 8H), 4.1- 4.2 (m, 12H), 4.32 (t, ³*J* = 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, ³*J* = 14 Hz, 2H), 7.11 (d, ³*J* = 8 Hz, 2H), 7.2-7.7 (m, 20H), 7.75 (d, ³*J* = 14 Hz, 2H), 8.10 (s, 1H). MS (MALDI-TOF): M⁺ = 1918.987 (calcd for C₅₉H₆₄N₅O₃: 1918.983).

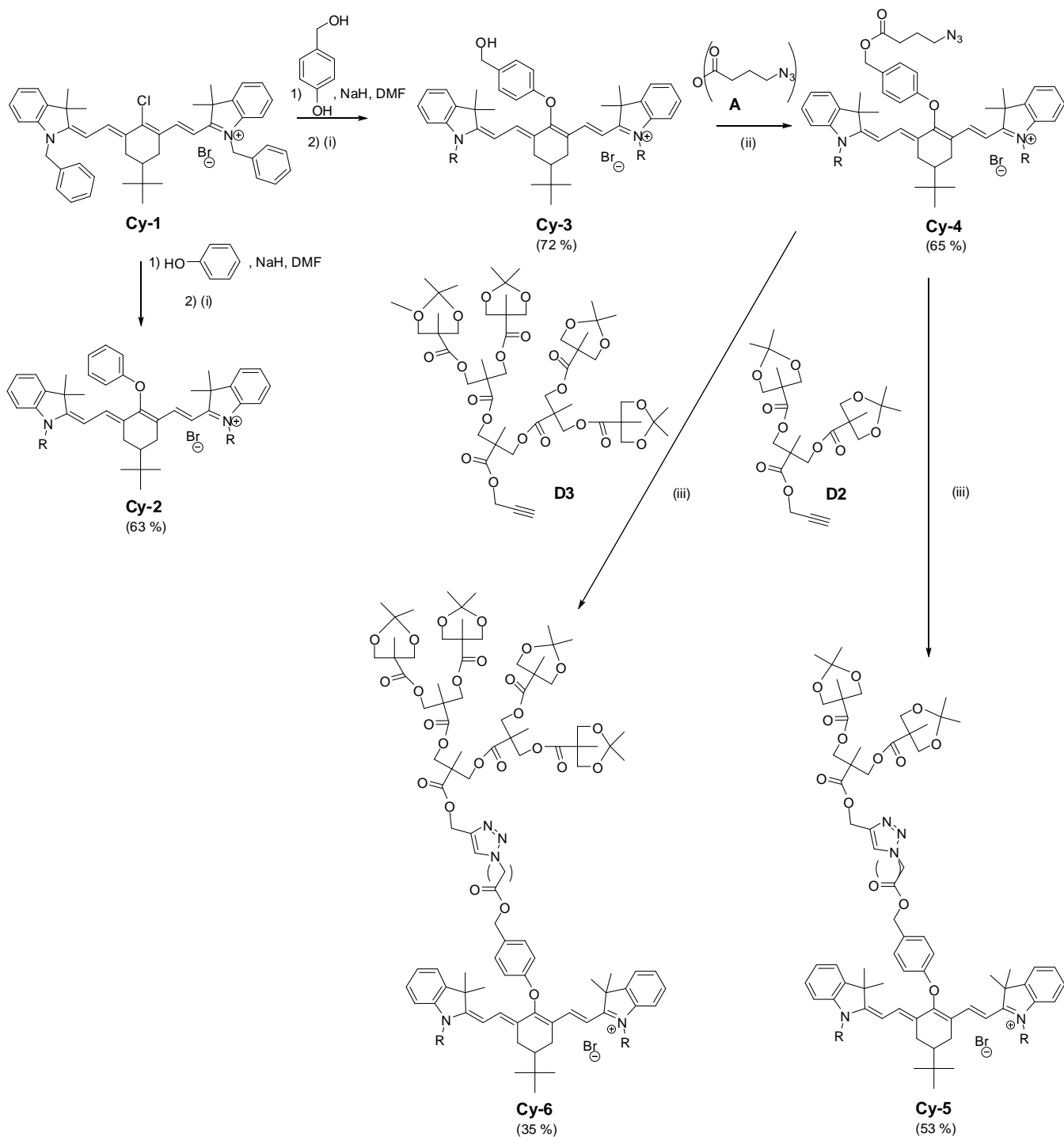
Acknowledgments

Authors thank the DGA and the Ecole Doctorale de Chimie de Lyon for a grant to P.A.B and the Polymer Factory Sweden AB for chemicals support.

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11. Dendrons **D2** and **D3** were kindly provided by the Polymer Factory Sweden AB (www.polymerfactory.com).



Scheme 1 : Reagent and conditions: (i) DMF, RT, 6 h, (ii) DMAP, DCM, RT, 12 h (65 %), (iii) CuSO₄, sodium ascorbate, THF-water, 50°C, 48 h



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

Table 1. Photophysical data in dichloromethane solution

Compound	λ_{max} (nm)	ϵ_{max} (L.mol ⁻¹ .cm ⁻¹)	λ_{em} (nm)	Th^a (J.cm ⁻²)	T_{min}^b (%)
Cy-1 ^c	794	350000	817	0.4 ± 0.2	70 ± 5
Cy-2	778	190000	802	0.4 ± 0.2	70 ± 5
Cy-5	778	210000	803	0.4 ± 0.2	70 ± 5
Cy-6	778	170000	800	-	-

^a Th 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 reference 2a

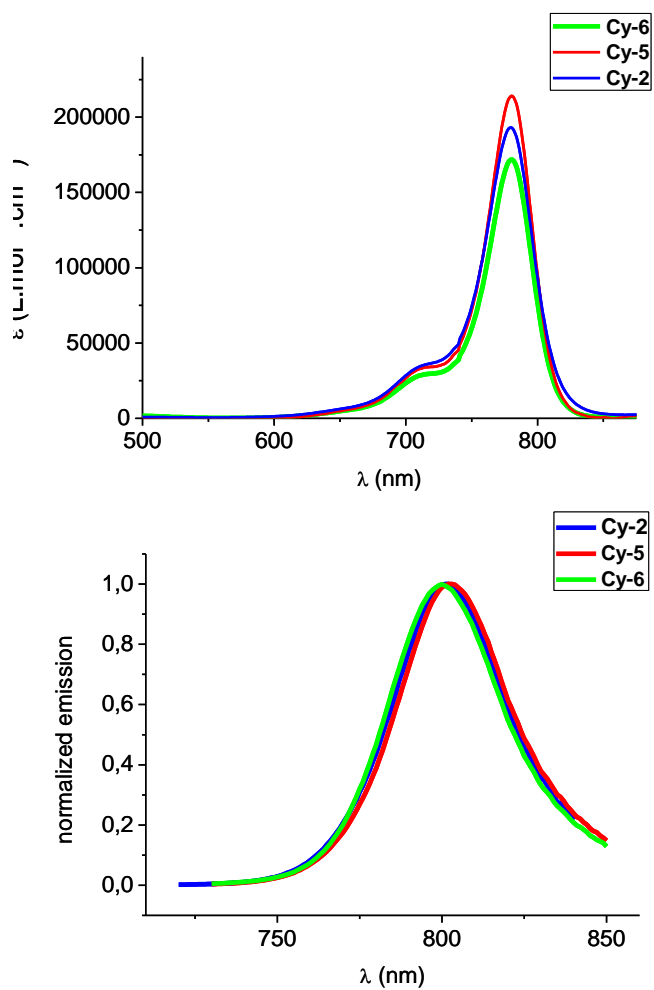


Figure 2. Absorption (top) and emission (bottom) spectra in DCM.

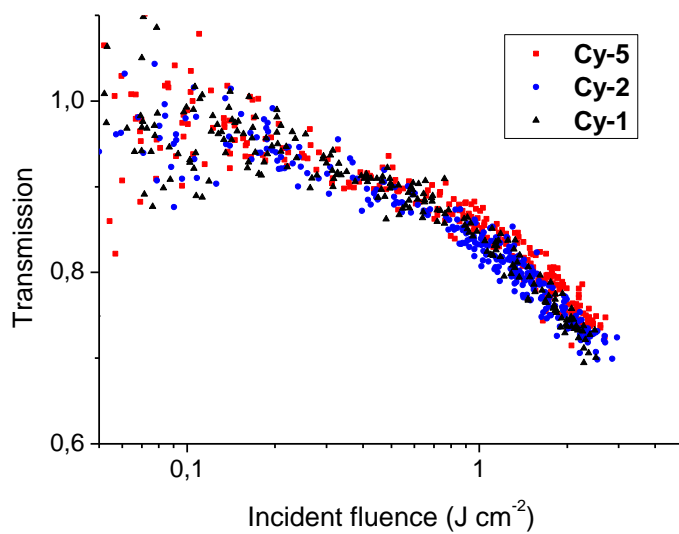


Figure 3. Nonlinear transmission curves at 1420 nm in DCM solution ($c = 0.1 \text{ mol.L}^{-1}$)