Supplementary Material (ESI) for Chemical Communications
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Gold Nanoparticles Synthesis and Stabilization via New "Clicked" Polyethyleneglycol Dendrimers

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ELECTRONIC SUPPLEMENTARY INFORMATION

General procedure for the synthesis of the new "clicked" PEG dendrimers:

The azido-terminated dendrimer (1 eq.) and the alkyne dendron (1.5 eq. *per* branch) were dissolved in THF. At 0°C, $CuSO_4$ was added (2 eq. *per* branch, 1M water solution), followed by the dropwise addition of a freshly prepared solution of sodium ascorbate (4 eq. *per* branch, 1M water solution) in order to set a 1:1 (THF/water) ratio. The solution was allowed to stir for 12h at 25°C under N_2. After removing THF under vacuum, CH_2Cl_2 and an aqueous ammonia solution were added. The mixture was allowed to stir for 10 min. in order to remove all the Cu^{II} trapped inside the dendrimer as $[Cu(NH_3)_6]^{2+}$. The organic phase was washed twice with water, dried with sodium sulfate, and the solvent was removed under vacuum. The product was precipitated with MeOH/ether in order to remove the excess dendron.

Equation for the measurement of the diffusion coefficients by ^{1}H NMR

The goal of this series of experiments is to measure the diffusion coefficients (noted D) of G_0-27-TEG, G_1-81-TEG and G_2-243-TEG by ^{1}H NMR.

First, the measurement of D allows to calculate the hydrodynamic diameter of a molecule. Then, the ^{1}H NMR experiment focuses on the diffusion that is mathematically treated according to a DOSY process (Diffusion Ordered SpectroscopY) in order to obtain the equivalent of a spectral chromatography. The objective is to measure the size of the molecules in solution by ^{1}H NMR.

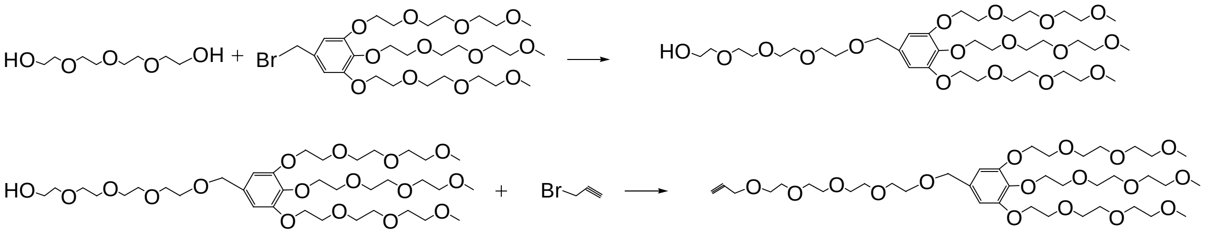
The dendrimers are considered as spherical molecular objects, and characterized by an apparent diffusion coefficient. The application of the Stokes-Einstein law gives an estimate of the diameter of the molecule.

Stokes-Einstein law:

$D = K_BT / 6\pi\eta r_H$

D: diffusion constant; K_B: Boltzman’s constant; T: temperature (K); η: solvent viscosity; r_H: hydrodynamic radius of the species.

Synthesis and characterization of the alkyne dendron



The tris-triethylene glycol dendron (1 g, 1.57 mmol) and the tetraethylene glycol (2.95 g, 15.7 mmol) were introduced in a Schlenck, and dry THF (50 mL) was added. NaH (108 mg, 2.7 mmol) was added to the solution. The mixture was stirred for 12 hours at 50°C. At the end of the reaction, water was added, then THF was removed. The product was extracted with CH_2Cl_2 and purified by chromatography (MeOH). 1g of a yellow oil was obtained (83% yield).

The tris-triethylene glycol tetraethylene glycol dendron (600 mg, 0.65 mmol) and dry THF (50 mL) were introduced in a Schlenck, and NaH (47 mg, 1.95 mmol) was added at 0°C. Propargyl bromide (155 mg, 1.3 mmol) was added to the solution. The mixture was stirred for 2 hours at 0°C, then 2 hours at 25°C. At the end of the reaction, water was added, then THF and excess propargyl bromide were removed under vacuum. The product was extracted with CH_2Cl_2 yielding 600 mg of a yellow oil (95% yield).

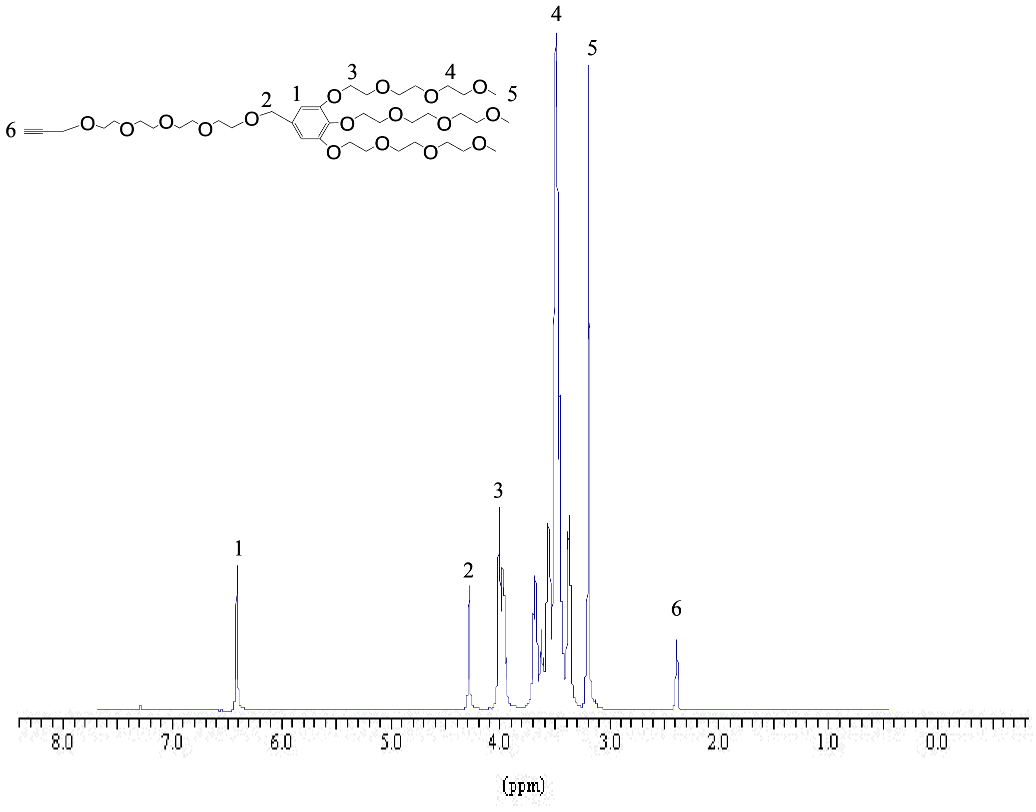
^{1}H NMR ($CDCl_3$, 250MHz): 6.39 (2H, C*H*-arom. extern), 4.26 (2H, O-C*H*$_2$-arom. extern), 3.98 (4H, C*H*$_2$O-arom. extern and C*H*$_2$-alkyne), 3.46 (30H, OC*H*$_2$C*H*$_2$O), 3.17 (9H, C*H*$_3$O), 2.36 (1H, C-C*H* alkyne) **(see the spectrum page 4)**

^{13}C NMR ($CDCl_3$, 62 MHz): 152.41 (*C*q-O arom.), 137.50 (*C*q-CH_2 arom.), 133.63 (Cq-*C*H2-O), 106.87 (*C*H arom.), 79.54 (*C*q alkyne), 74.75 (*C*H alkyne), 70.46 (O-*C*H$_2$), 58.74(O-*C*H$_3$), 58.13 (*C*H$_2$-alkyne) **(see the spectrum page 5)**

Infrared υ_{alkyne}: 2100 cm^{-1} **(see the spectrum page 6)**

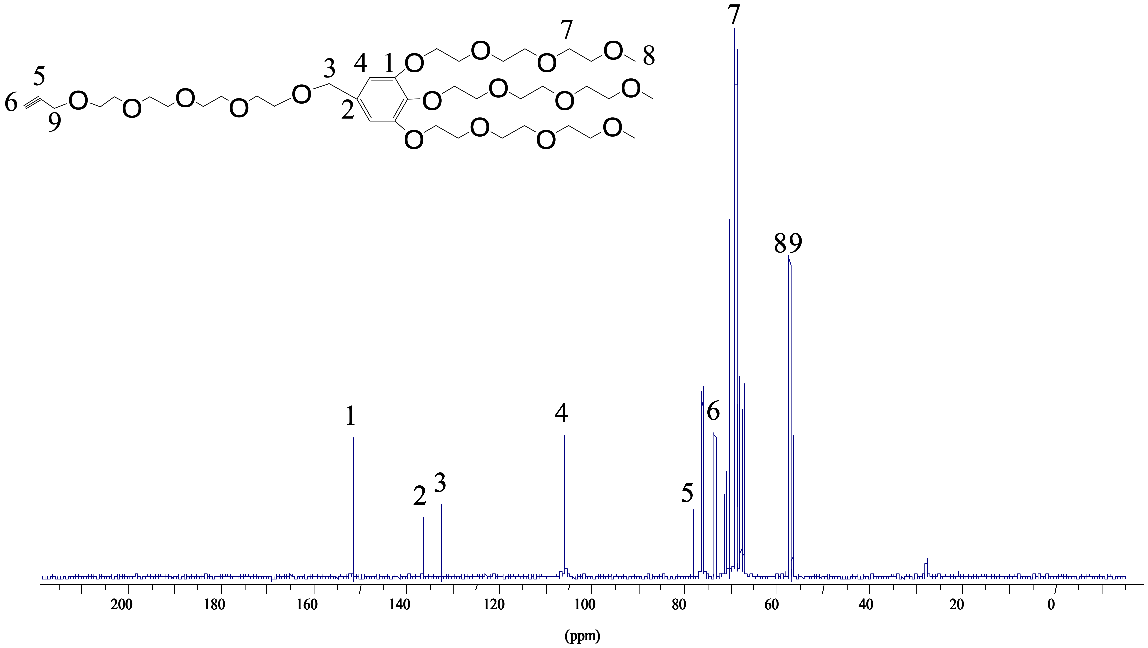
Maldi TOF : Calc. for $C_{39}H_{68}O_{17}$: 808; found: 831 (MNa^+) **(see the spectrum page 6)**

^{1}H NMR spectrum of the alkyne dendron



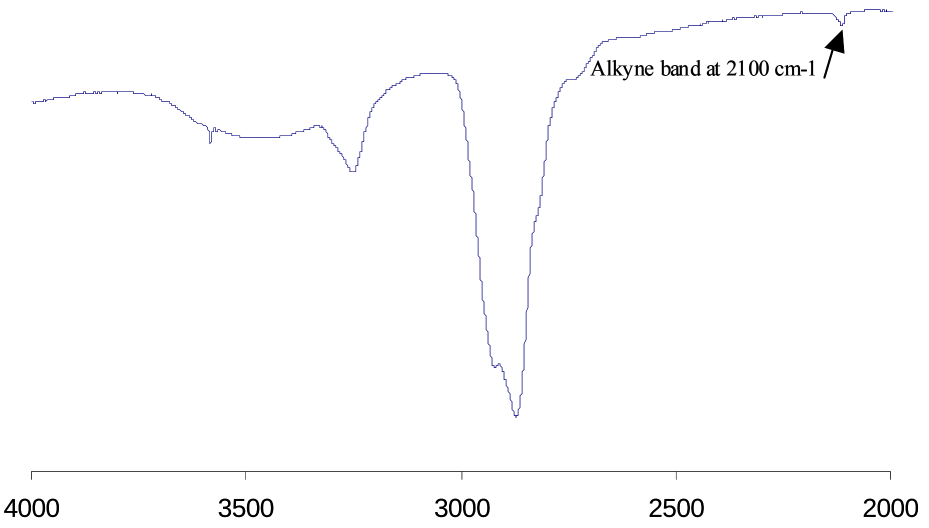
^{1}H NMR (CDCl$_3$, 250MHz): 6.39 (2H, CH-arom. extern), 4.26 (2H, O-CH_2-arom. extern), 3.98 (4H, CH_2O-arom. extern and CH_2-alkyne), 3.46 (30H, OCH_2CH_2O), 3.17 (9H, CH_3O), 2.36 (1H, C-CH alkyne).

^{13}C NMR spectrum of the alkyne dendron



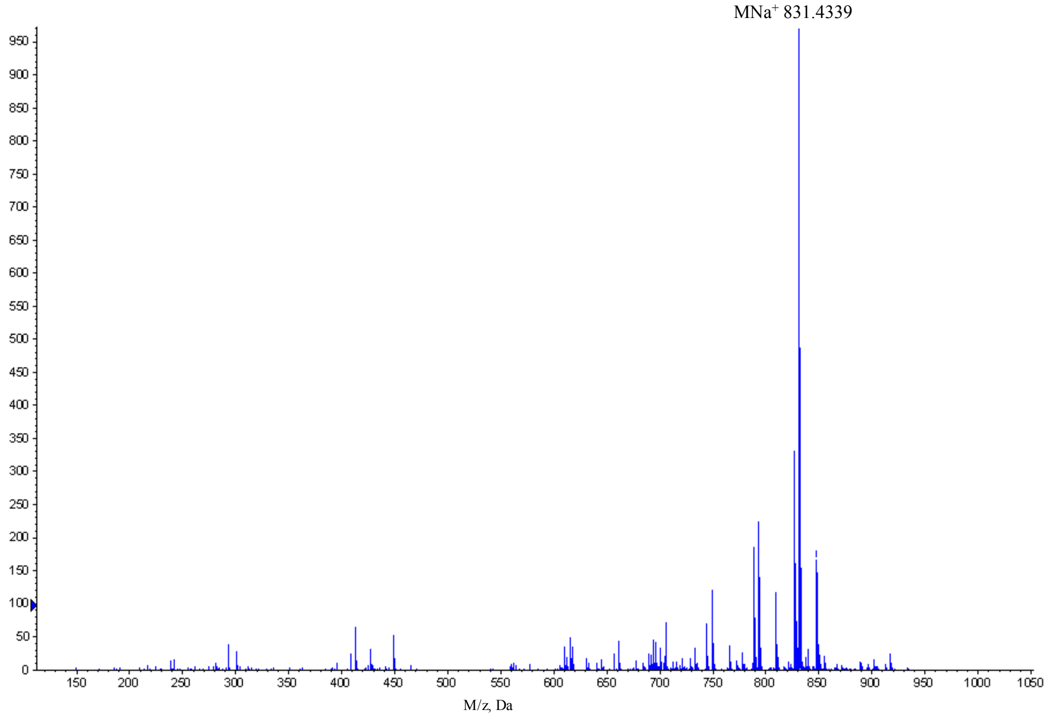
^{13}C NMR ($CDCl_3$, 62 MHz): 152.41 (*C*q-O arom.), 137.50 (*C*q-CH_2 arom.), 133.63 (Cq-*C*H2-O), 106.87 (*C*H arom.), 79.54 (*C*q alkyne), 74.75 (*C*H alkyne), 70.46 (O-CH_2), 58.74(O-CH_3), 58.13 (CH_2-alkyne).

IR spectrum of the alkyne dendron



Infrared υ_{alkyne}: 2100 cm^{-1}.

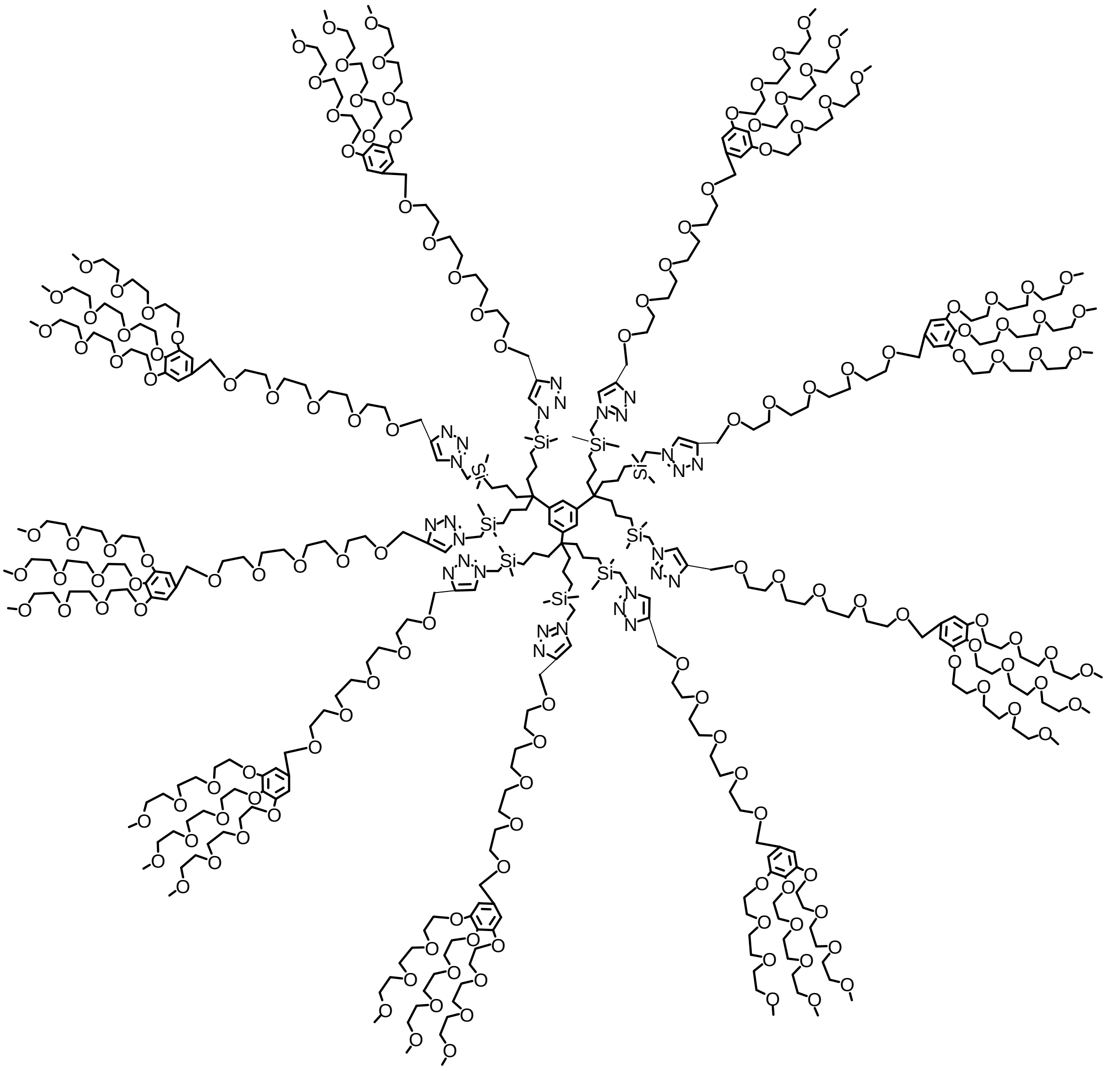
Mass spectrum of the alkyne dendron



Maldi TOF : Calc. for $C_{39}H_{68}O_{17}$: 808; found: 831 (MNa^+).

G_0-27-PEG

Mw = 8 787 g.mol^{-1}



Characterization of G_0-27-TEG

^{1}H NMR ($CDCl_3$, 250MHz): 7.45 (9H, C*H*-triazole), 6.93 (36H, C*H*-arom. intern), 6.56 (18H, C*H*-arom. extern), 4.62 (18H, triazole-$C\mathit{H}_2$-0), 4.43 (18H, O-$C\mathit{H}_2$-arom. extern), 4.11 (72H, $C\mathit{H}_2O$-arom. extern and Si-$C\mathit{H}_2$-triazole), 3.64 (414H, $OC\mathit{H}_2C\mathit{H}_2O$), 3.37 (27H, $C\mathit{H}_3O$), 1.59 (18H, $C\mathit{H}_2CH_2CH_2Si$), 1.07 (18H, $CH_2C\mathit{H}_2CH_2Si$), 0.60 (18H, $CH_2CH_2C\mathit{H}_2Si$), 0.006 (54H, $Si(C\mathit{H}_3)_2$). **(see the spectrum page 9)**

^{13}C NMR ($CDCl_3$, 62 MHz): 151.62 (*C*H, extern arom.), 144.48 (C_q of triazole), 136.83 (*C*q, arom. core), 132.75 (*C*q, arom. extern), 123.52 (*C*H of triazole and arom. core), 106.23 (C_qCH_2O), 69.54 ($O\mathit{C}H_2\mathit{C}H_2O$), 63.53 (triazole-$\mathit{C}H_2$-O), 58.00 ($\mathit{C}H_3O$), 53.38 (OCH2-arom.extern), 43.77 ($\mathit{C}H_2CH_2CH_2Si$), 42.7 ($SiC\mathit{H}_2$-triazole), 40.93 (*C*q-arom.intern), 17.82 ($CH_2\mathit{C}H_2CH_2Si$), 14.90 ($CH_2CH_2\mathit{C}H_2Si$), -4.84 ($Si(\mathit{C}H_3)_2$). **(see the spectrum page 10)**

DOSY : D = 1.16 (± 0.1) x 10^{-10} m²/s
Rh = 4.9 (± 0.1) nm
(D: diffusion coefficient; Rh : hydrodynamic radius) **(see DOSY spectrum page 11)**

IR: no alkyne and azide bands **(see the spectrum page 12)**

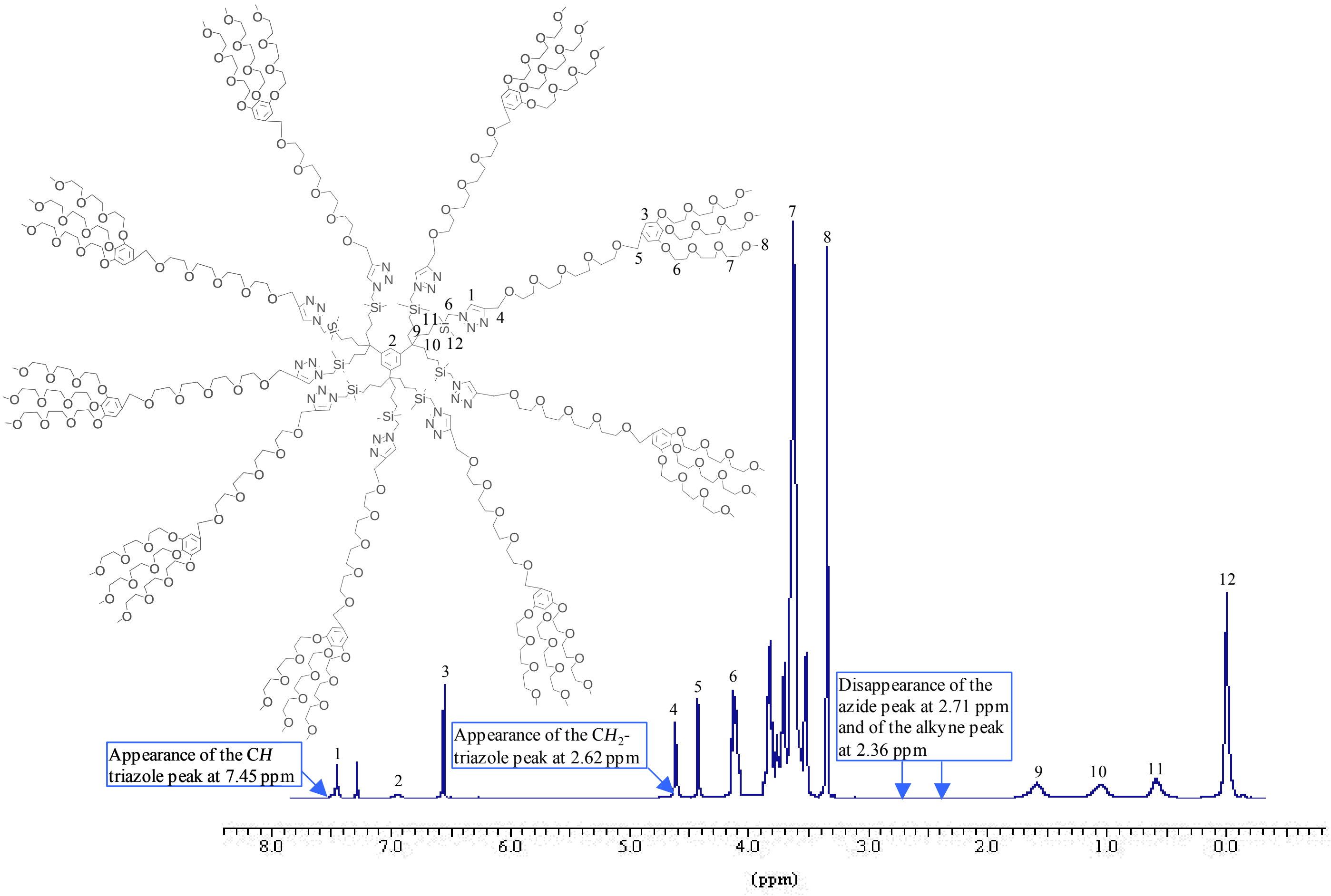
SEC : **(see the spectrum page 23)**

MALDI-TOF mass spectrum: Calc. for $C_{414}H_{741}O_{153}N_{27}Si_9$: 8798; found: 8824 ($MNa^+$). **(see the spectrum page 12)**

Elemental Analysis: Anal. Calc. for $C_{414}H_{741}O_{153}N_{27}Si_9$: C 56.52, H 8.49; found: C 56.31, H 8.49

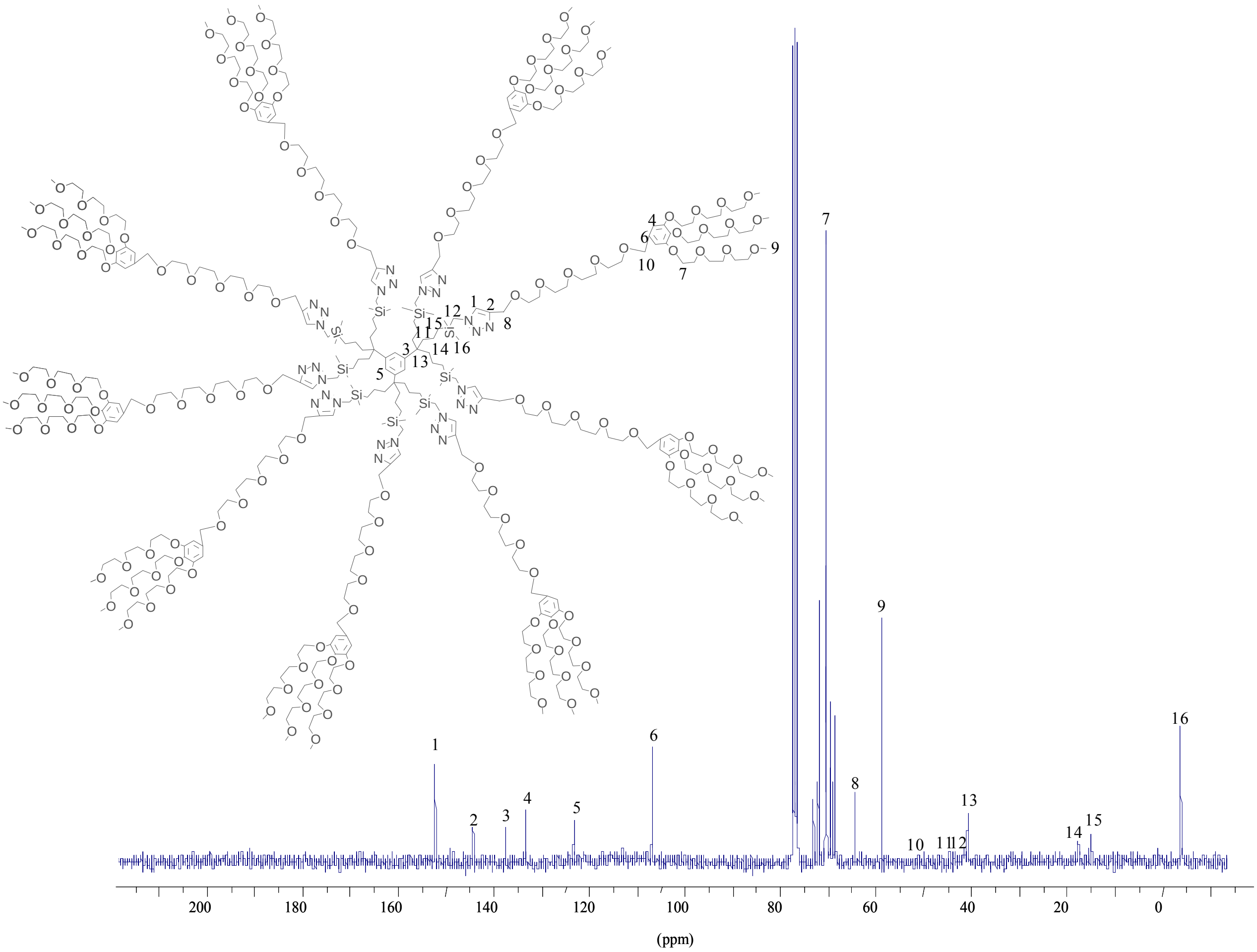
Light scattering : Rh = 4.5 (± 0.4) nm

^{1}H NMR spectrum of G_0-27-PEG



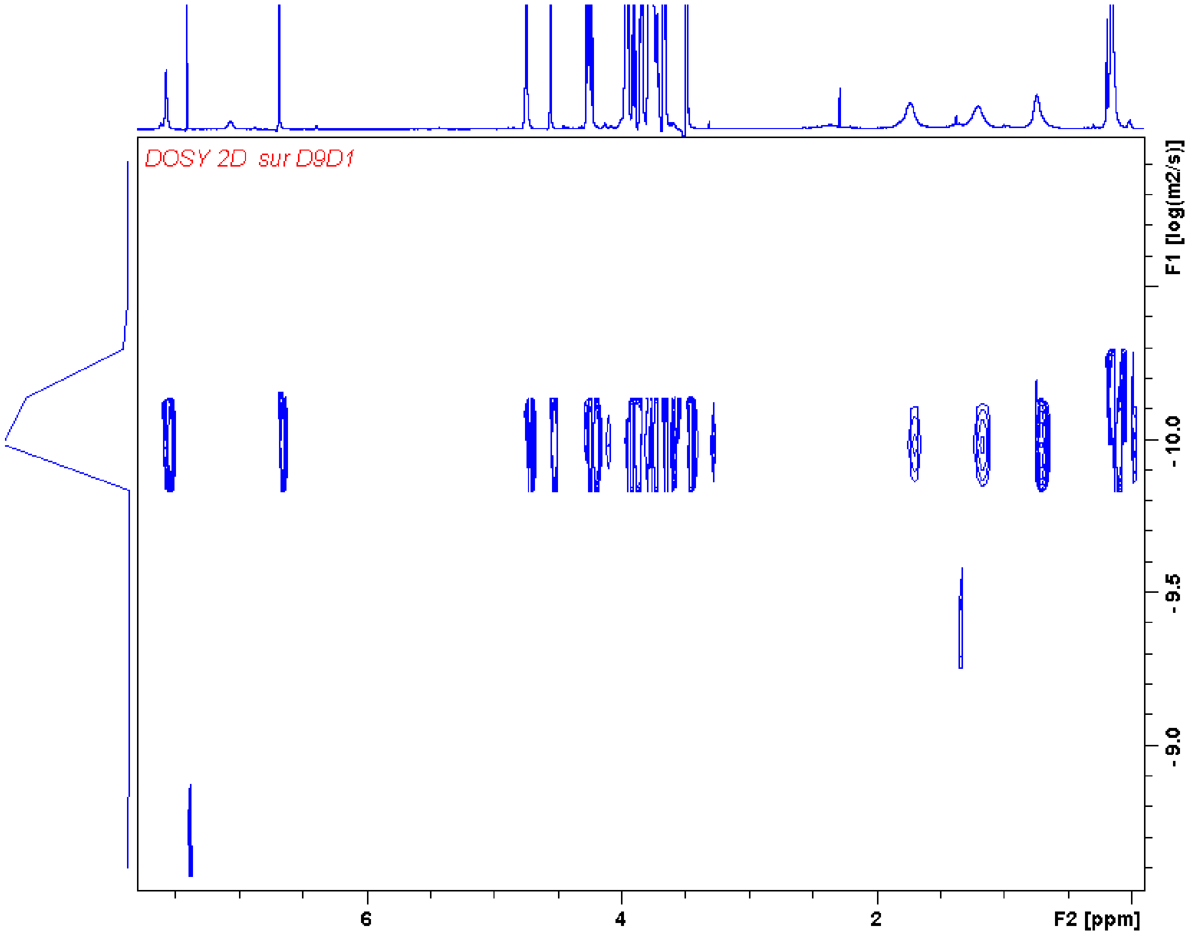
^{1}H NMR ($CDCl_3$, 250MHz): 7.45 (9H, C*H*-triazole), 6.93 (36H, C*H*-arom. intern), 6.56 (18H, C*H*-arom. extern), 4.62 (18H, triazole-CH_2-0), 4.43 (18H, O-CH_2-arom. extern), 4.11 (72H, CH_2O-arom. extern and Si-CH_2-triazole), 3.64 (414H, OCH_2CH_2O), 3.37 (27H, CH_3O), 1.59 (18H, CH_2CH$_2$CH$_2$Si), 1.07 (18H, CH$_2$CH_2CH$_2$Si), 0.60 (18H, CH$_2$CH$_2$CH_2Si), 0.006 (54H, Si(CH_3)$_2$).

^{13}C NMR spectrum of G_0-27-PEG



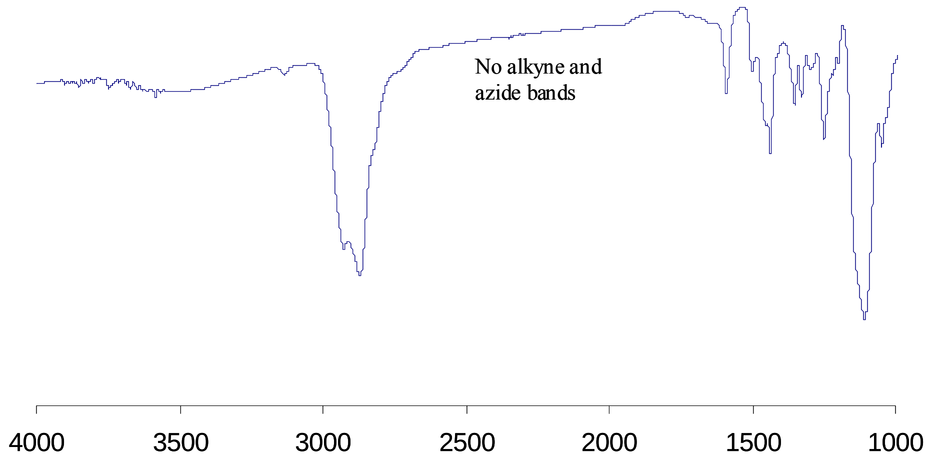
^{13}C NMR ($CDCl_3$, 62 MHz): 151.62 (*C*H, extern arom.), 144.48 (C_q of triazole), 136.83 (*C*q, arom. core), 132.75 (*C*q, arom. extern), 123.52 (*C*H of triazole and arom. core), 106.23 (C_qCH_2O), 69.54 (OCH_2CH_2O), 63.53 (triazole-CH_2-O), 58.00 (CH_3O), 53.38 (OCH2-arom.extern), 43.77 ($CH_2CH_2CH_2Si$), 42.7 ($SiCH_2$-triazole), 40.93 (*C*q-arom.intern), 17.82 ($CH_2CH_2CH_2Si$), 14.90 ($CH_2CH_2CH_2Si$), -4.84 ($Si(CH_3)_2$).

DOSY spectrum of G_0-27-PEG

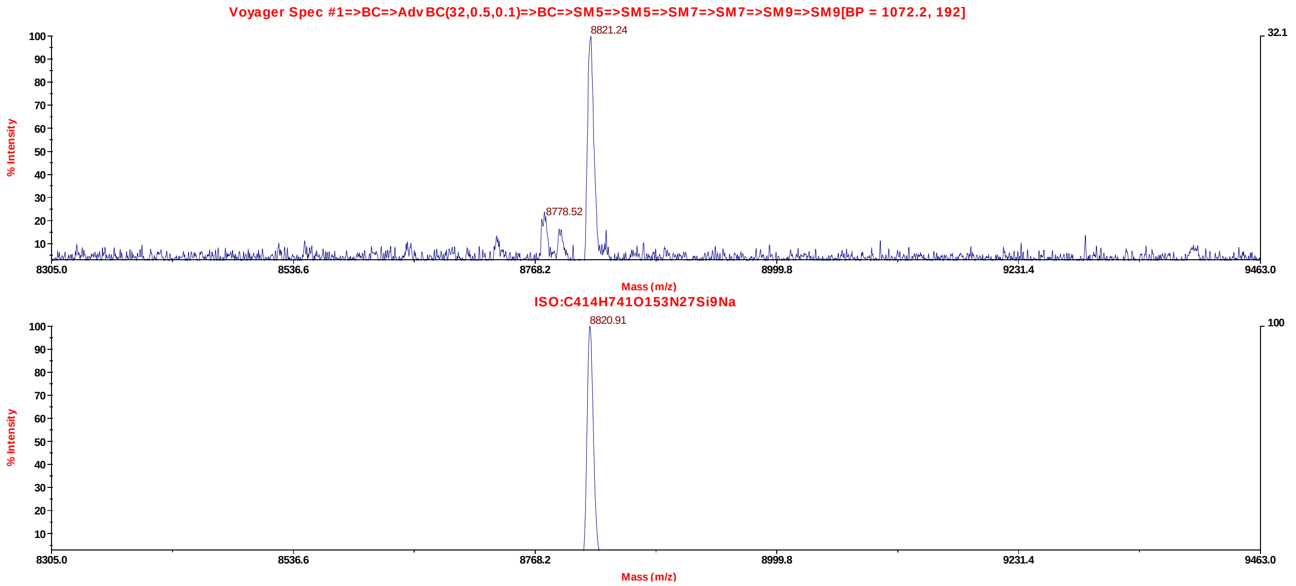


DOSY : D = 1.16 (± 0.1) x 10^{-10} m²/s
Rh = 4.9 (± 0.1) nm
(D: diffusion coefficient; Rh : hydrodynamic radius) .

IR spectrum of G_0-27-PEG



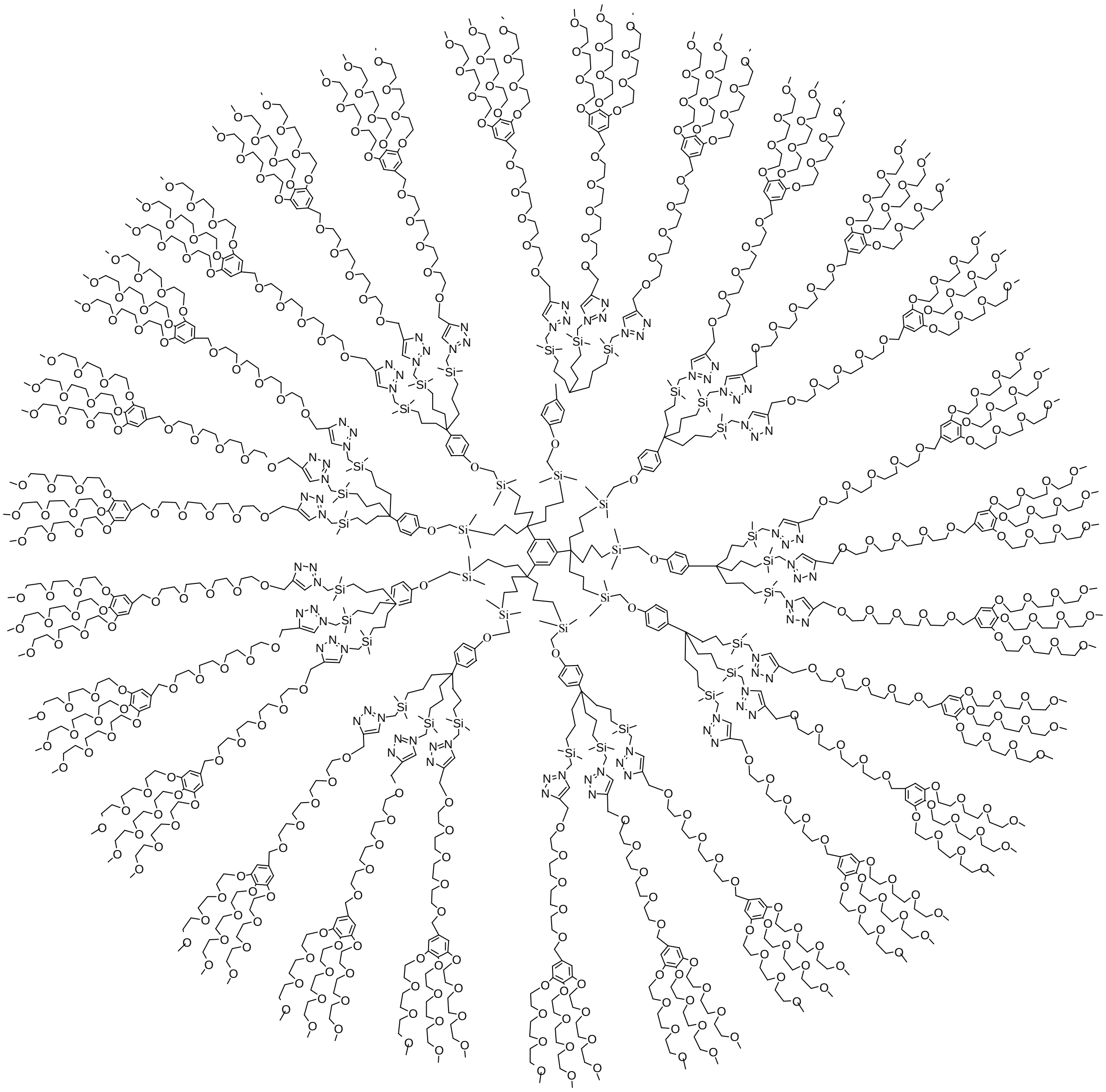
MALDI-TOF mass spectrum of G_0-27-PEG



MALDI-TOF: Calc. for $C_{414}H_{741}O_{153}N_{27}Si_9$: 8798; found: 8821.25 ($MNa^+$).

G₁-81-PEG

Mw = 28 462 g.mol^{-1}



Characterization of G_1-81-TEG

^{1}H NMR ($CDCl_3$, 250MHz): 7.41 (27H, C*H*-triazole), 6.97 (144H, C*H*-arom. intern), 6.56 (54H, C*H*-arom. extern), 4.62 (54H, triazole-CH_2-0), 4.43 (54H, O-CH_2-arom. extern), 4.13 (126H, CH_2O-arom. extern and Si-CH_2-triazole), 3.64 (1242H, OCH_2CH_2O), 3.37 (81H, CH_3O), 1.59 (54H, CH_2CH$_2$CH$_2$Si), 1.09 (54H, CH$_2$CH_2CH$_2$Si), 0.57 (54H, CH$_2$CH$_2$CH_2Si), 0.06 (216H, Si(CH_3)$_2$) **(see the spectrum page 15)**

^{13}C NMR ($CDCl_3$, 62 MHz): 152.60 (*C*H, extern arom.), 144.48 (C_q of triazole), 137.79 (*C*q, arom. core), 133.75 (*C*q, arom. extern), 126.12 and 113.9 (*C*H-arom. Intern), 123.52 (*C*H of triazole and arom. core), 107.23 (C_qCH$_2$O), 70.66 (O*C*H$_2$*C*H$_2$O), 69.11 (Si-*C*H$_2$-O), 63.53 (triazole-*C*H$_2$-O), 58.99 (*C*H$_3$O), 53.38 (O*C*H$_2$-arom.extern), 43.77 (*C*H$_2$CH$_2$CH$_2$Si), 42.7 (SiCH_2-triazole), 40.93 (*C*q-arom.intern), 17.82 (CH$_2$*C*H$_2$CH$_2$Si), 14.90 (CH$_2$CH$_2$*C*H$_2$Si), -4.84 (Si(*C*H$_3$)$_2$) **(see the spectrum page 16)**

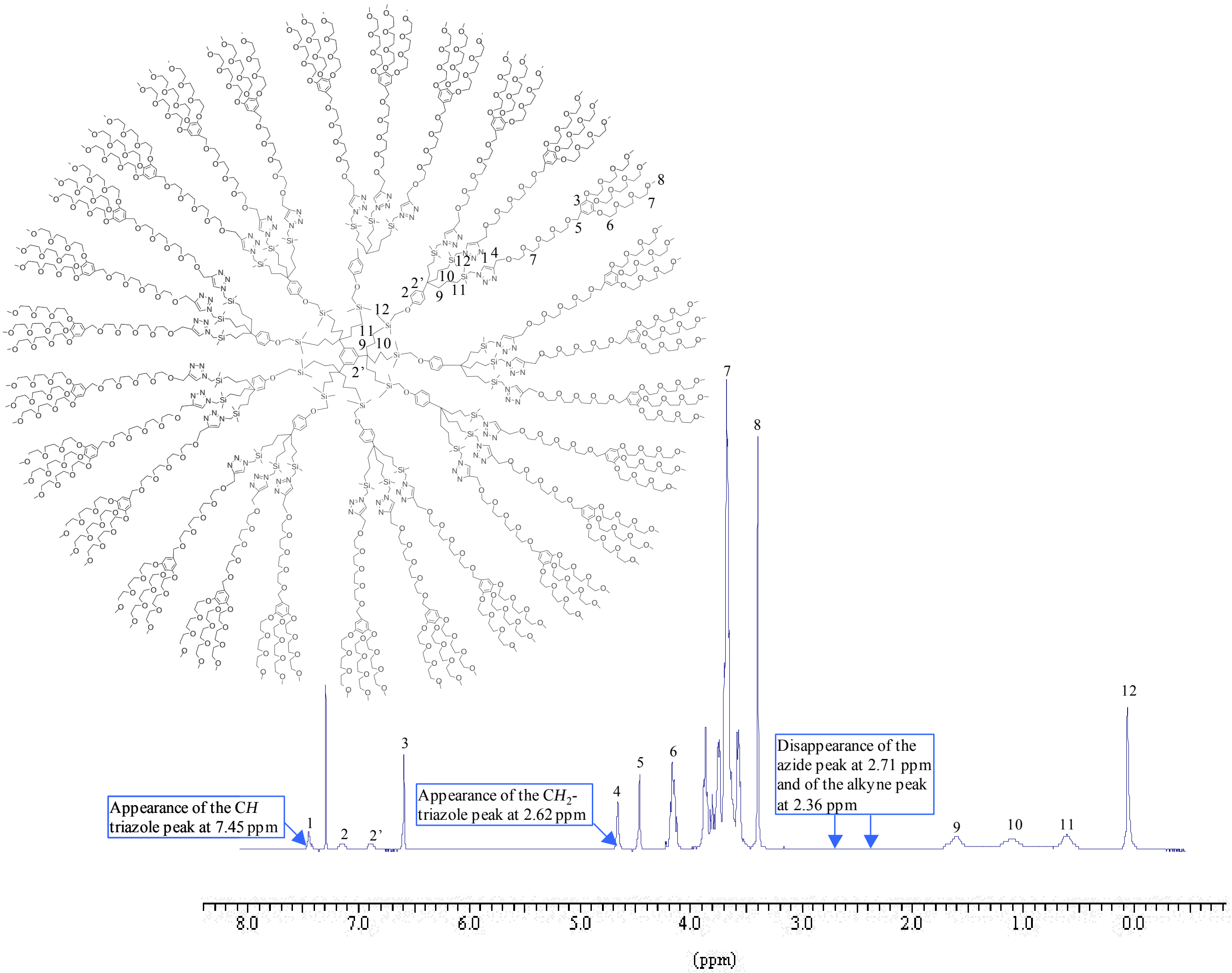
DOSY : D = 5.94 (± 0.1) x 10^{-11} m²/s
Rh = 9.7 (± 0.7) nm
(D: diffusion coefficient; Rh : hydrodynamic radius)**(see the DOSY spectrum page 17)**

IR: no alkyne and azide bands **(see the spectrum page 17)**

SEC : **(see the spectrum page 23)**

Light scattering : Rh = 9.1 (± 0.6) nm

^{1}H NMR spectrum of G_1-81-PEG



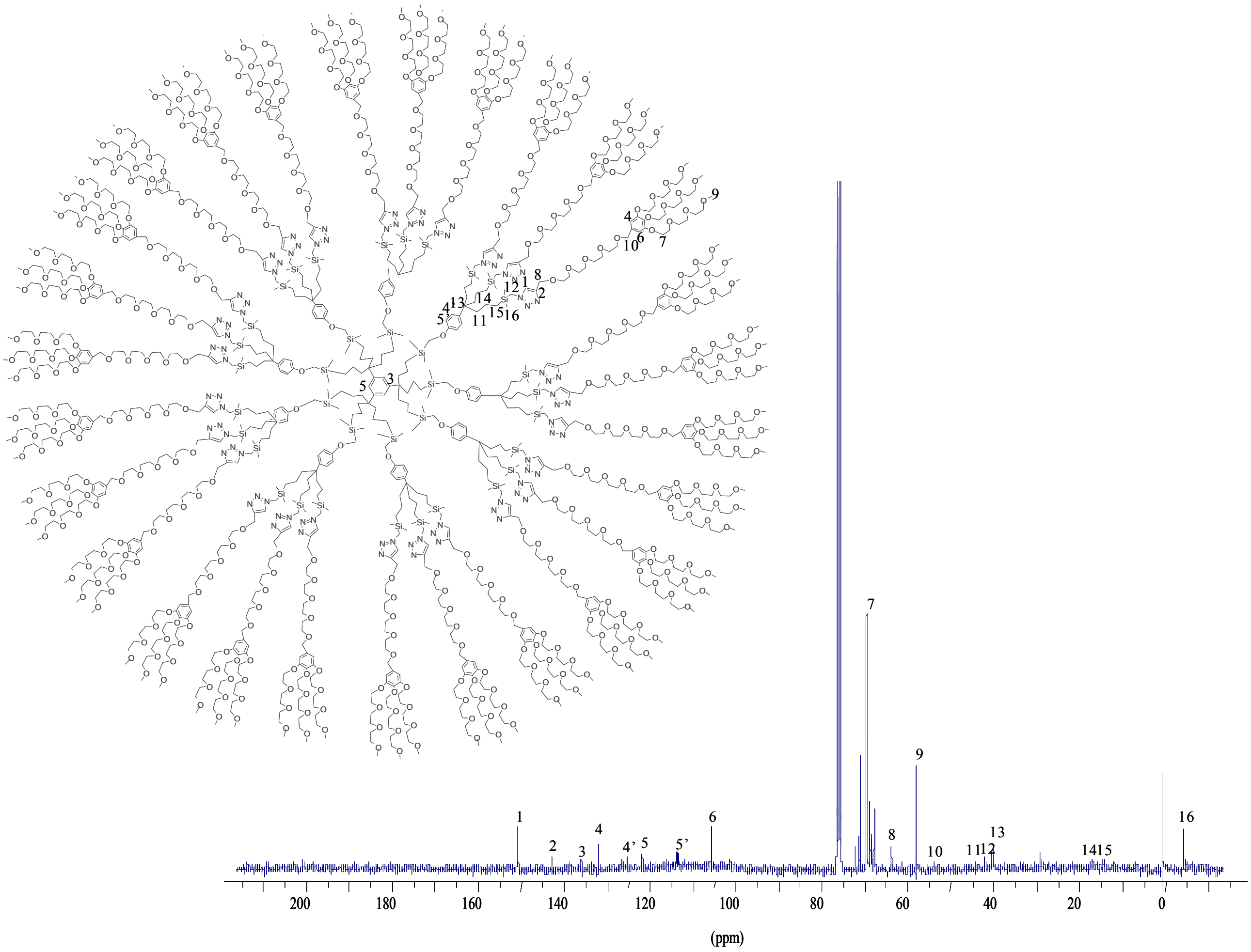
Appearance of the C*H* triazole peak at 7.45 ppm

Appearance of the C*H*$_2$-triazole peak at 2.62 ppm

Disappearance of the azide peak at 2.71 ppm and of the alkyne peak at 2.36 ppm

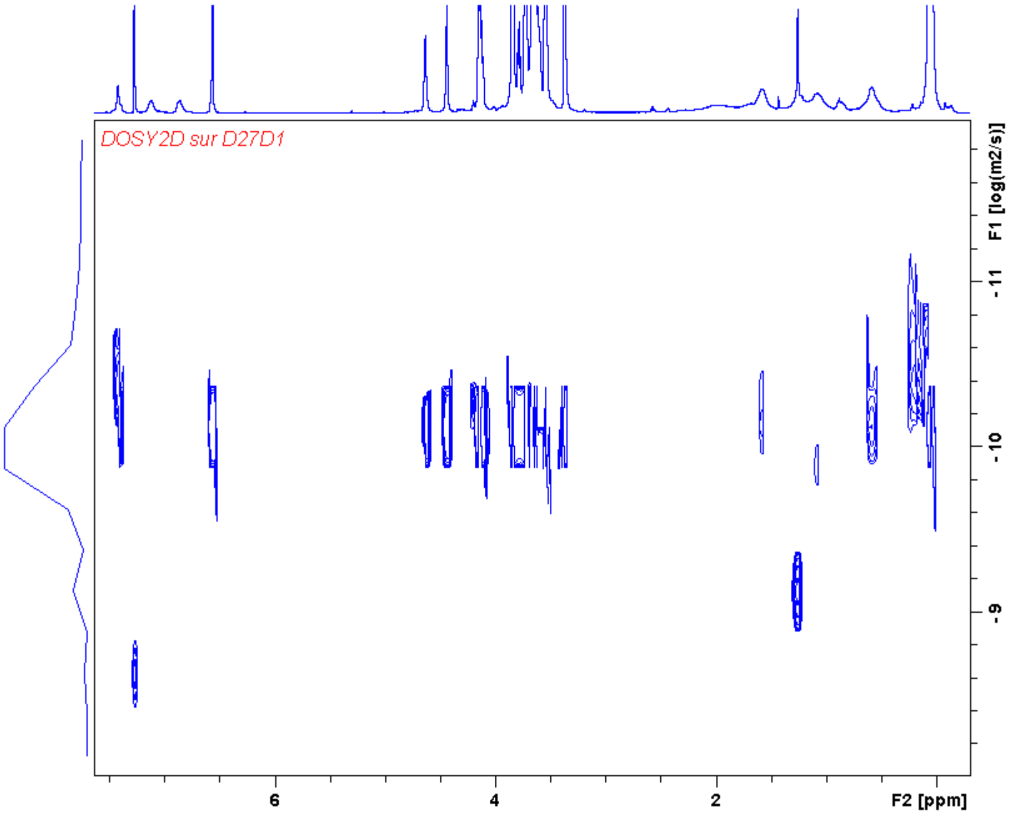
^{1}H NMR (CDCl$_3$, 250MHz): 7.41 (27H, C*H*-triazole), 6.97 (144H, C*H*-arom. intern), 6.56 (54H, C*H*-arom. extern), 4.62 (54H, triazole-C*H*$_2$-0), 4.43 (54H, O-C*H*$_2$-arom. extern), 4.13 (126H, C*H*$_2$O-arom. extern and Si-C*H*$_2$-triazole), 3.64 (1242H, OC*H*$_2$C*H*$_2$O), 3.37 (81H, C*H*$_3$O), 1.59 (54H, C*H*$_2$CH$_2$CH$_2$Si), 1.09 (54H, CH$_2$C*H*$_2$CH$_2$Si), 0.57 (54H, CH$_2$CH$_2$C*H*$_2$Si), 0.06 (216H, Si(C*H*$_3$)$_2$).

^{13} C NMR spectrum of G_1-81-PEG



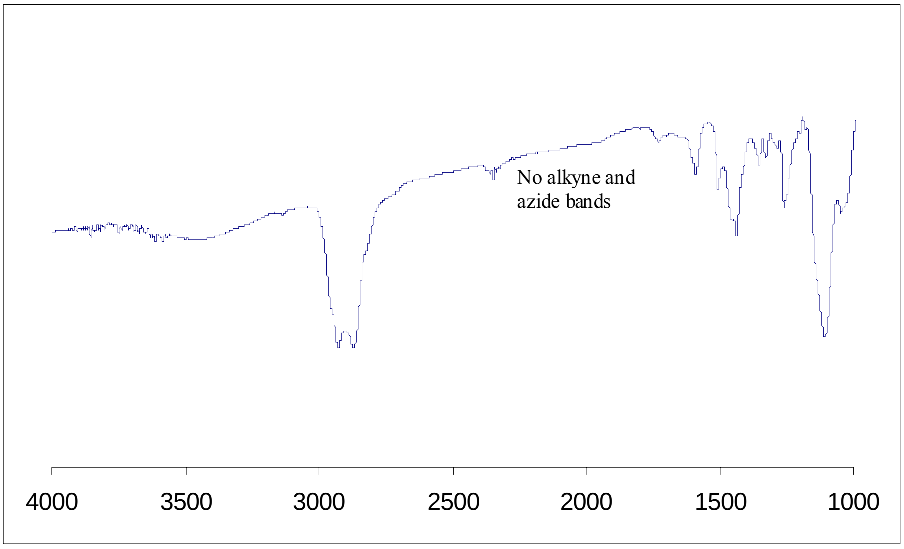
^{13}C NMR ($CDCl_3$, 62 MHz): 152.60 (*C*H, extern arom.), 144.48 (C_q of triazole), 137.79 (*C*q, arom. core), 133.75 (*C*q, arom. extern), 126.12 and 113.9 (*C*H-arom. Intern), 123.52 (*C*H of triazole and arom. core), 107.23 ($C_q$$CH_2O$), 70.66 (O*C*H$_2$*C*H$_2$O), 69.11 (Si-*C*H$_2$-O), 63.53 (triazole-*C*H$_2$-O), 58.99 (*C*H$_3$O), 53.38 (O*C*H$_2$-arom.extern), 43.77 (*C*H$_2$CH$_2$CH$_2$Si), 42.7 (SiC*H*$_2$-triazole), 40.93 (*C*q-arom.intern), 17.82 (CH$_2$*C*H$_2$CH$_2$Si), 14.90 (CH$_2$CH$_2$*C*H$_2$Si), -4.84 (Si(*C*H$_3$)$_2$).

DOSY spectrum of G_1-81-PEG



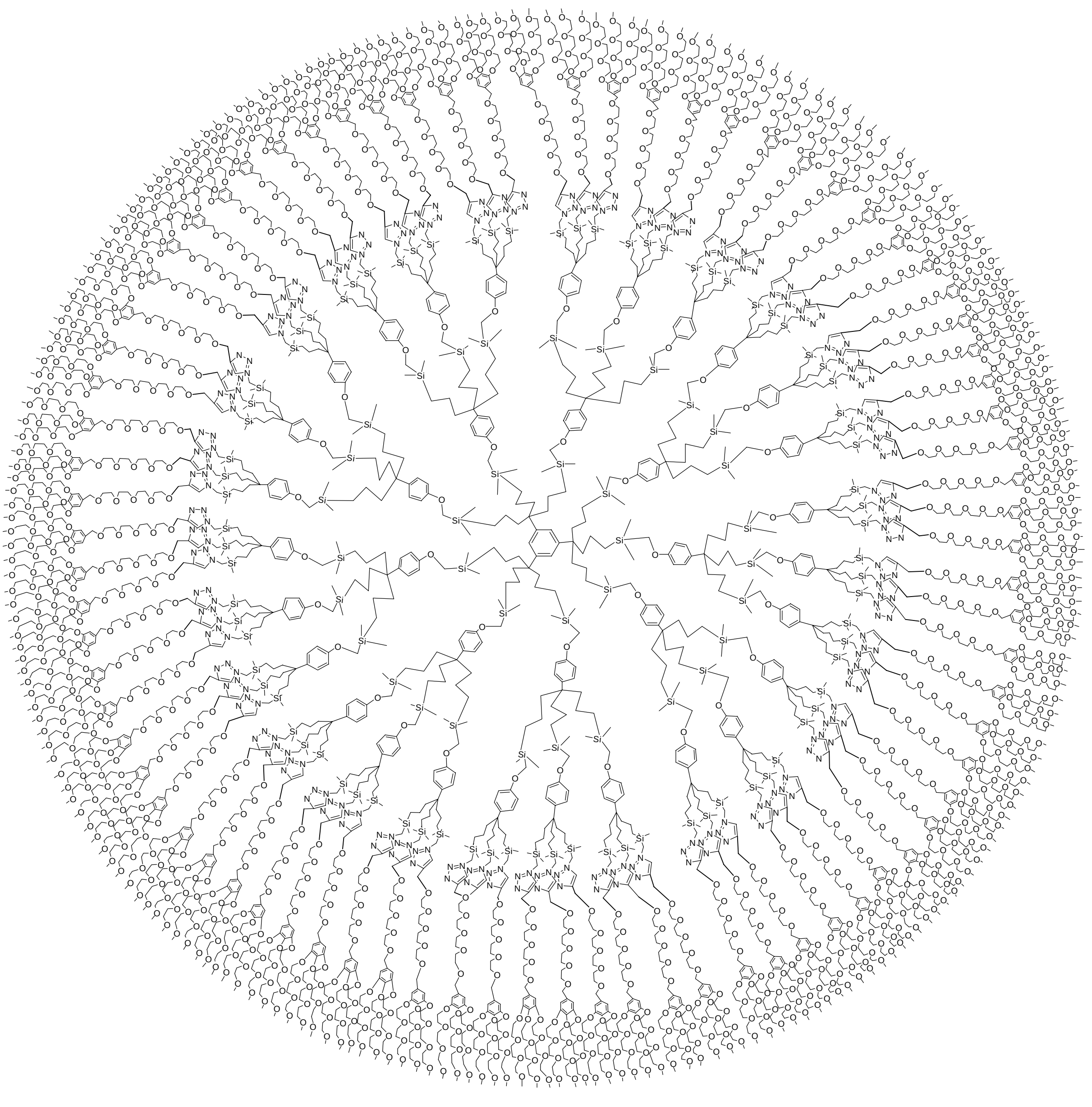
DOSY : D = 5.94 (± 0.1) x 10^{-11} m²/s
Rh = 9.7 (± 0.7) nm
(D: diffusion coefficient; Rh : hydrodynamic radius)

IR spectrum of G_1-81-PEG



G$_2$-243-PEG

Mw = 80 319 g.mol^{-1}



Characterization of G_2-243-TEG

^{1}H NMR ($CDCl_3$, 250MHz): 7.41 (81H, C*H*-triazole), 7.09 (117H, C*H*-arom. intern), 6.56 (234H, C*H*-arom. extern), 4.61 (162H, triazole-CH_2-0), 4.44 (234H, O-CH_2-arom. extern), 4.11 (396H, CH_2O-arom. extern and Si-CH_2-triazole), 3.64 (3726H, OCH_2CH_2O), 3.37 (243H, CH_3O), 1.59 (234H, $CH_2CH_2CH_2$Si), 1.09 (234H, $CH_2CH_2CH_2$Si), 0.54 (234H, $CH_2CH_2CH_2$Si), 0.06 (702H, Si(CH_3)$_2$) **(see the spectrum page 20)**

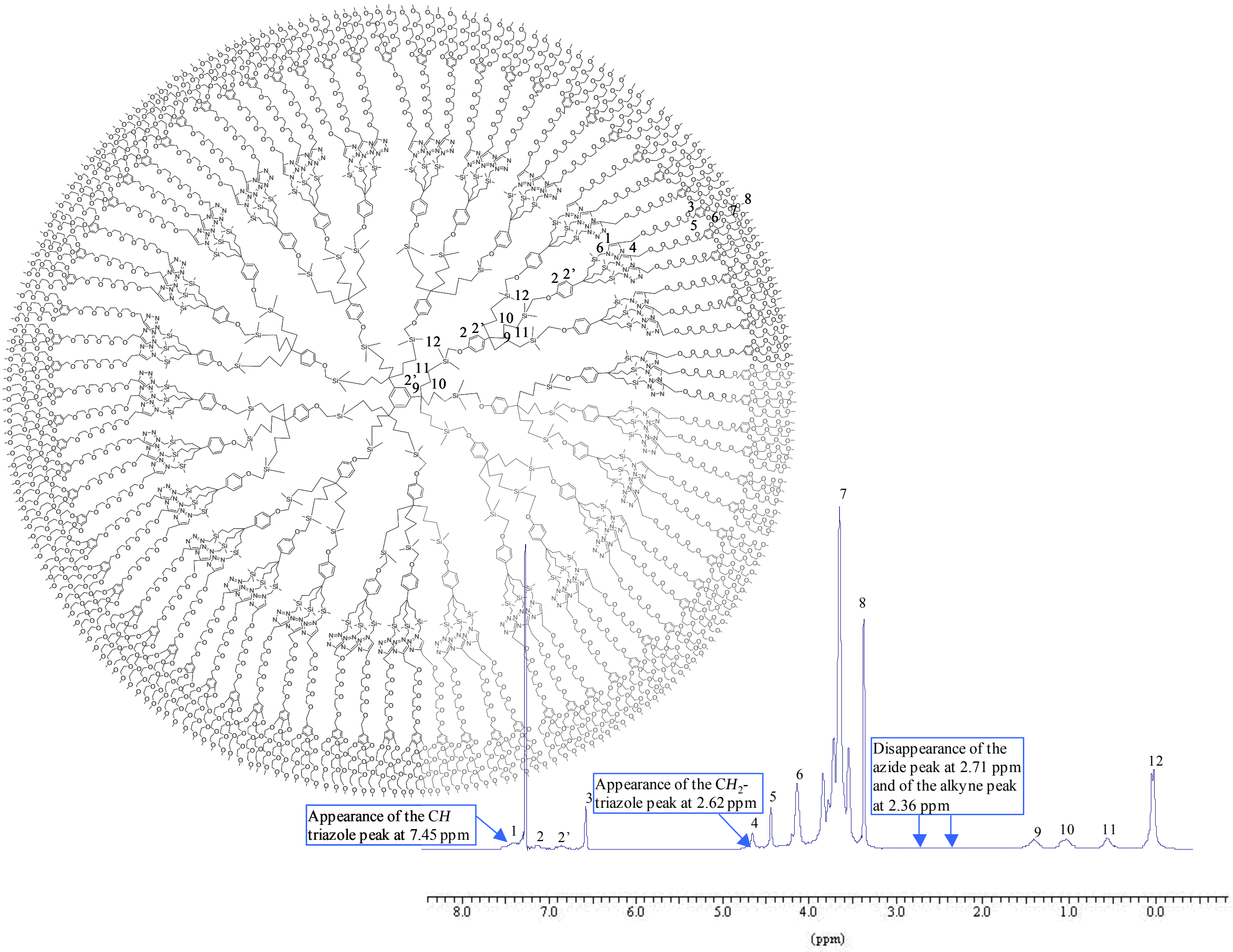
^{13}C NMR ($CDCl_3$, 62 MHz): 151.60 (*C*H, extern arom.), 144.48 (C_q of triazole), 136.80 (*C*q, arom. core), 132.78 (*C*q, arom. extern), 126.12 and 113.94 (*C*H-arom. intern) 123.52 (*C*H of triazole and arom. core), 106.23 ($C_q$$CH_2$O), 69.13 (Si-$CH_2$-O), 68.73 (O$CH_2CH_2$O), 63.53 (triazole-$CH_2$-O), 57.39 ($CH_3$O), 53.38 (O$CH_2$-arom.extern), 43.77 ($CH_2CH_2CH_2$Si), 42.7 (Si$CH_2$-triazole), 40.93 (*C*q-arom.intern), 17.82 ($CH_2CH_2CH_2$Si), 14.90 ($CH_2CH_2CH_2$Si), -4.84 (Si(CH_3)$_2$) **(see the spectrum page 21)**

IR: no alkyne and azide bands **(see the spectrum page 22)**

SEC : **(see the spectrum page 23)**

Light scattering : Rh = 10 (±1) nm

^{1}H NMR spectrum of G$_2$-243-PEG



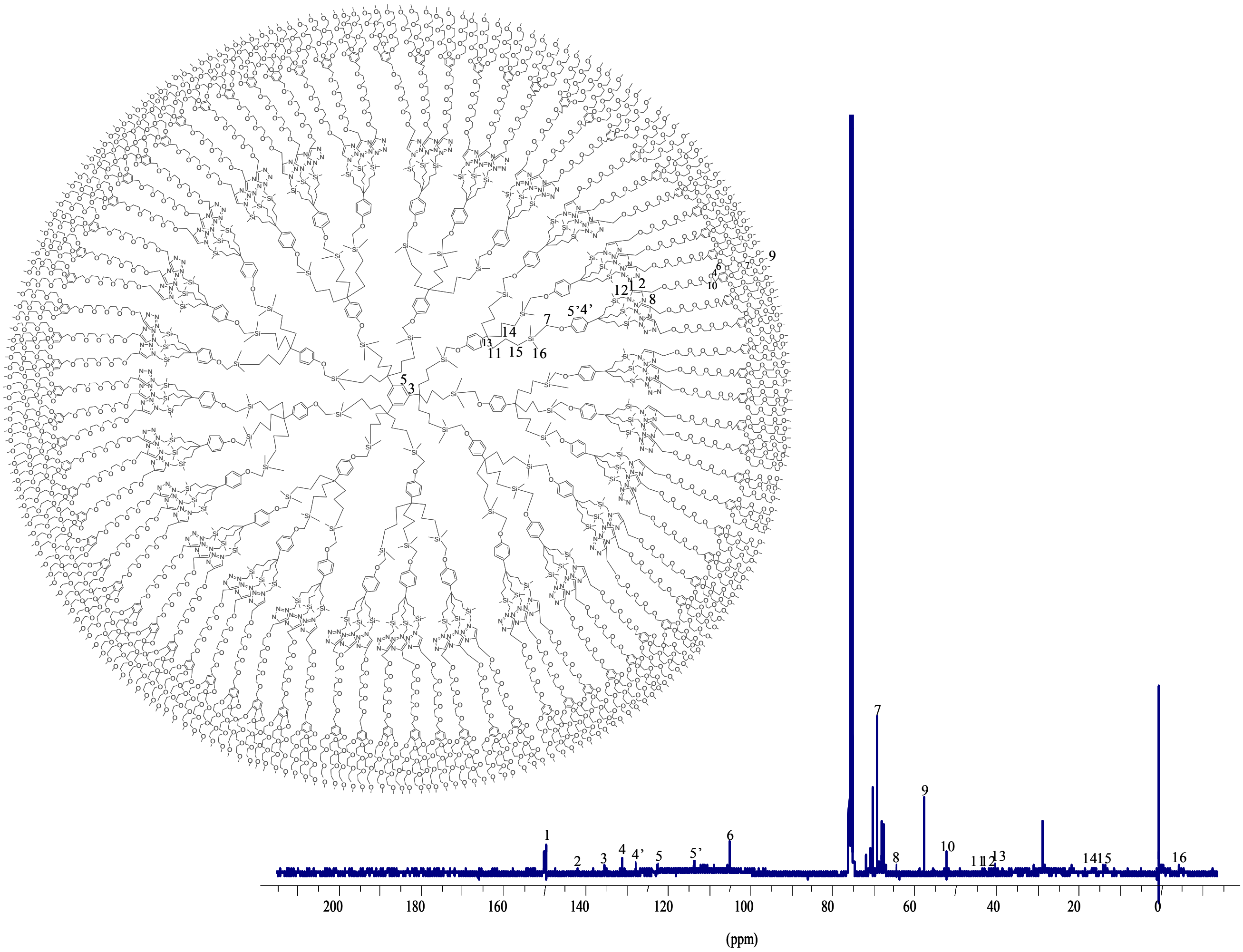
Appearance of the C*H* triazole peak at 7.45 ppm

Appearance of the CH_2-triazole peak at 2.62 ppm

Disappearance of the azide peak at 2.71 ppm and of the alkyne peak at 2.36 ppm

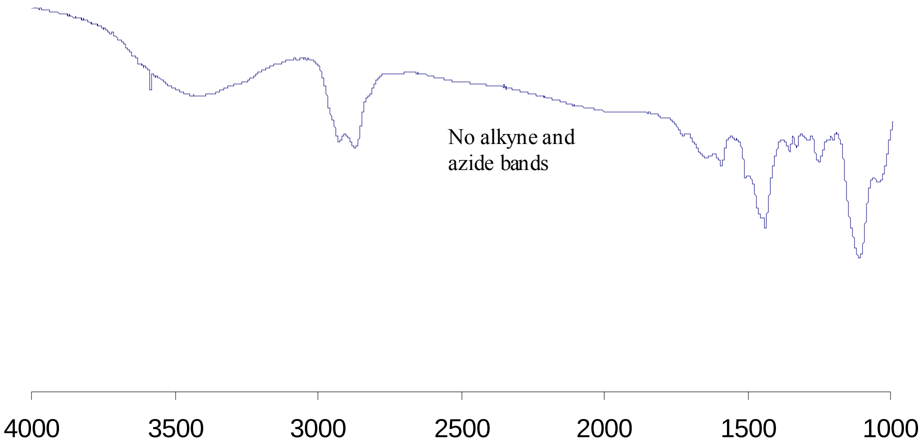
^{1}H NMR (CDCl$_3$, 250MHz): 7.41 (81H, C*H*-triazole), 7.09 (117H, C*H*-arom. intern), 6.56 (234H, C*H*-arom. extern), 4.61 (162H, triazole-CH_2-0), 4.44 (234H, O-CH_2-arom. extern), 4.11 (396H, CH_2O-arom. extern and Si-CH_2-triazole), 3.64 (3726H, OCH_2CH_2O), 3.37 (243H, CH_3O), 1.59 (234H, CH_2CH$_2$CH$_2$Si), 1.09 (234H, CH$_2$CH_2CH$_2$Si), 0.54 (234H, CH$_2$CH$_2$CH_2Si), 0.06 (702H, Si(CH_3)$_2$).

^{13}C NMR spectrum of G$_2$-243-PEG

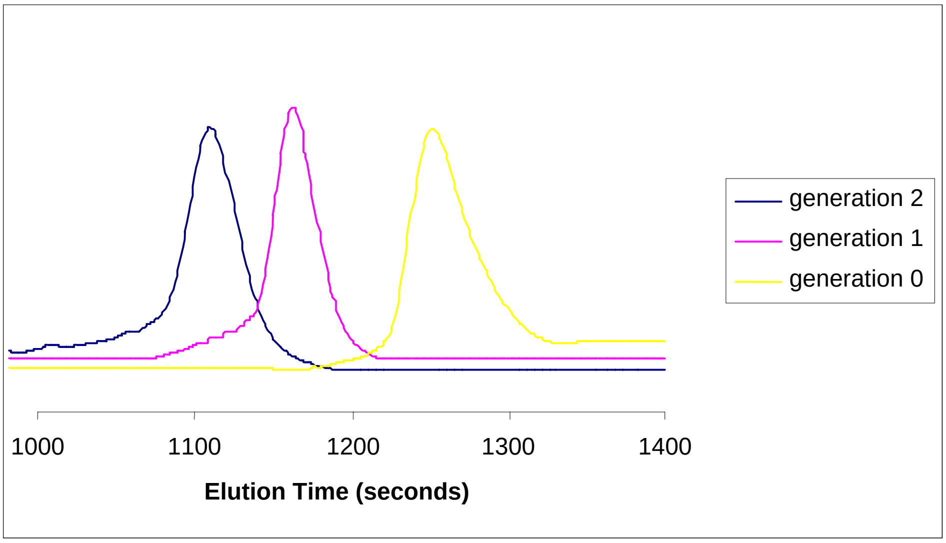


^{13}C NMR (CDCl$_3$, 62 MHz): 151.60 (*C*H, extern arom.), 144.48 (C_q of triazole), 136.80 (*C*q, arom. core), 132.78 (*C*q, arom. extern), 126.12 and 113.94 (*C*H-arom. intern) 123.52 (*C*H of triazole and arom. core), 106.23 (C_qCH$_2$O), 69.13 (Si-*C*H$_2$-O), 68.73 (O*C*H$_2$*C*H$_2$O), 63.53 (triazole-*C*H$_2$-O), 57.39 (*C*H$_3$O), 53.38 (O*C*H$_2$-arom.extern), 43.77 (*C*H$_2$CH$_2$CH$_2$Si), 42.7 (SiC*H*$_2$-triazole), 40.93 (*C*q-arom.intern), 17.82 (CH$_2$*C*H$_2$CH$_2$Si), 14.90 (CH$_2$CH$_2$*C*H$_2$Si), -4.84 (Si(*C*H$_3$)$_2$).

IR spectrum of G_2-243-PEG



Size Exclusion Chromatography (SEC) of the three generations of "click" dendrimers containing polyethyleneglycol tethers



Transmission Electron Microscopy (TEM)

The samples were prepared by placing a drop of 1.6 10^{-4} M solution (MeOH) of gold nanoparticles (concentration in mol Au) on a holey-carbon-coated Cu TEM grid.

General procedure for the preparation of AuNPs (these procedures are described using preparation of D-27-polyethylene glycol): 1 mL of a 1.14×10^{-4} M solution of dendrimer (1mg, 1.14×10^{-4} mmol) in MeOH was placed in a Schlenk flask under nitrogen.0.349 mL of a 2.94×10^{-3} M solution of $HAuCl_4$ (0.349 mg, 1.03x 10^{-3} mmol, 1 equiv. *per* triazole). 4.65 mL of MeOH was added to obtain a solution 2.21×10^{-4} M (in Au)
The solution was stirred for 1h and $NaBH_4$ wad added (0.39 mg, 1.03×10^{-2} mmol, 10 equiv. *per* Au), the yellow solution turned to golden brown indicating the nanoparticule formation.

Attempts to stabilize AuNPs by "click" dendrimers that do not contain PEG ligands

The stabilization of AuNPs was attempted using five others dendrimers. Four of them only contain triazolyl groups and do not contain any PEG, and the last one only contains PEG but no triazolyl groups.

"Click" dendrimers with 9, 27 and 81 allyl tethers and a "click" dendrimer with 27 phenyl tethers were used. All the syntheses and structures of these dendrimers are described in the following publication: "Click" Dendrimers: Synthesis, Redox Sensing of $Pd(OAc)_2$, and Remarkable Catalytic Hydrogenation Activity of Precise Pd Nanoparticles Stabilized by 1,2,3-Triazole-Containing Dendrimers by Catia Ornelas, Jaime Ruiz Aranzaes, Lionel Salmon, and Didier Astruc, and published in *Chem. Eur. J.* **2007**, *14*, 50.
The procedure used for the addition and reduction of $HAuCl_4$ in these dendrimers is the same one as that described page 24 of this ESI using a stoichiometric amount of $HAuCl_4$ vs. the dendrimer triazolyl groups. When $NaBH_4$ in methanol is added, the gold nanoparticles are formed but they precipitate after a few minutes.

A dendrimer containing 81 PEG tethers, but no triazolyl ligand (whose synthesis will be described latter) is used for comparison. The procedure used for the addition and reduction of $HAuCl_4$ in this dendrimer is the same as that described page 24 of this ESI with 81 equiv. Au *per* dendrimer. The result is similar to that obtained with the above dendrimers containing only triazolyl groups (this page), i.e. AuNPs immediately precipitate when $NaBH_4$ in methanol is added.

These five experiments support the fact that the presence of both the PEG and triazolyl groups in these dendrimers are essential for the stabilization of AuNPs.