Supporting Information

"Click" dendrimers as efficient nanoreactors in aqueous solvent: Pd nanoparticles stabilization for sub-ppm Pd catalysis of Suzuki-Miyaura reactions of aryl bromides

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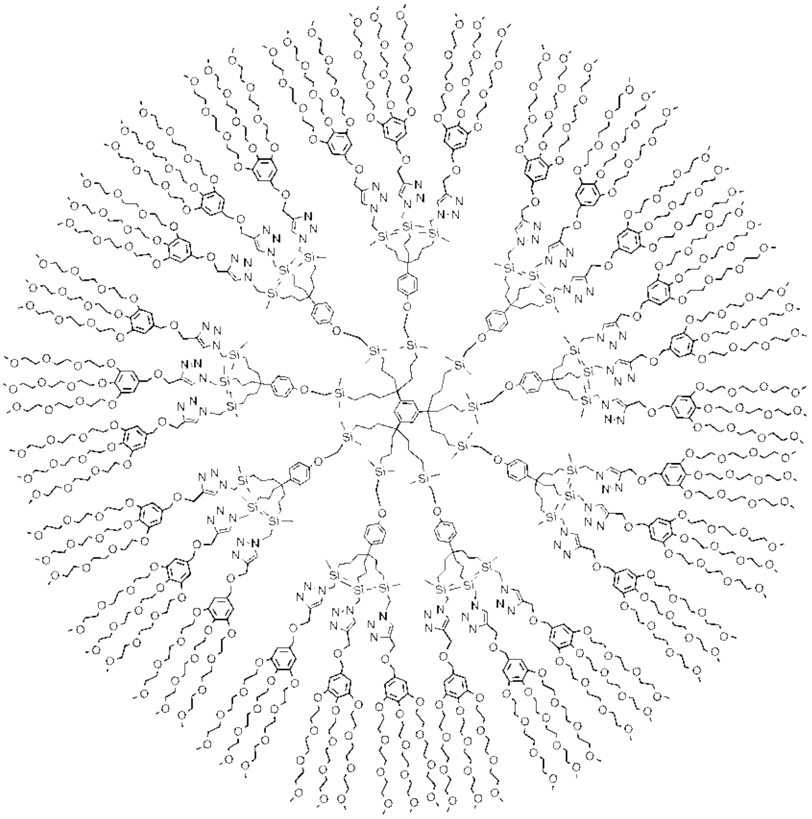
1. General data

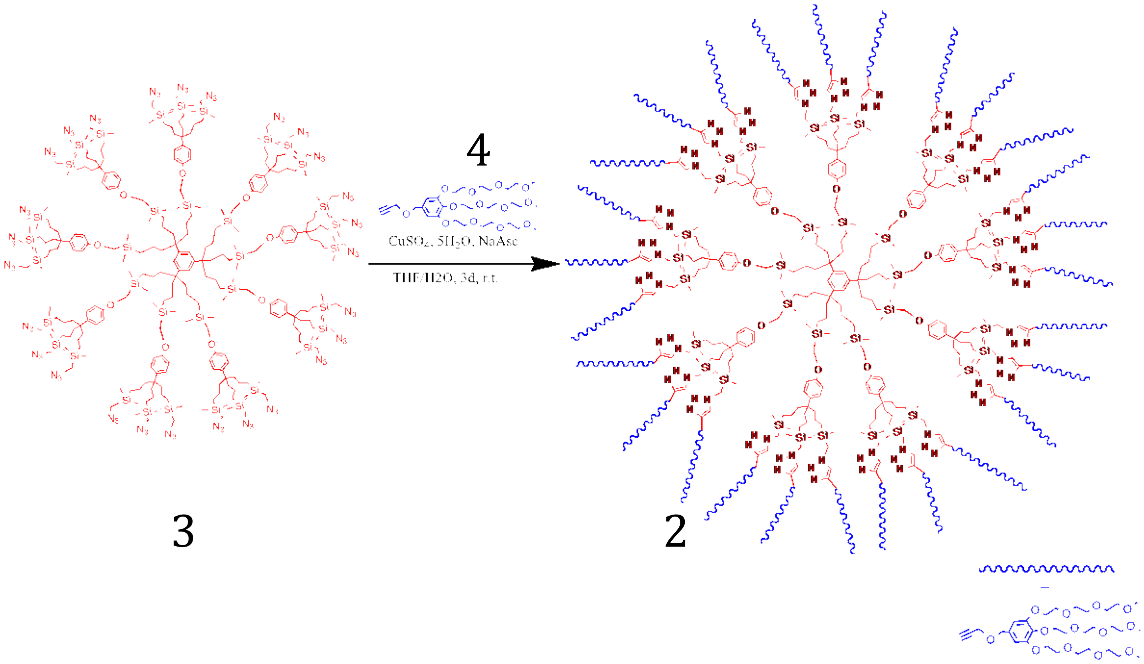
All the solvents (THF, ethanol…) and chemicals were used as received.
^{1}H NMR spectra and **^{13}C NMR** spectrum were recorded at 25°C with a Bruker AC 200 or 300 (200 or 300 MHz) spectrometer. All the chemical shifts are reported in parts per million (δ, ppm) with reference to Me_4Si (TMS) for the ^{1}H spectra.
The **UV-vis.** absorption spectra were measured with Perkin-Elmer Lambda 19 UV-vis.
The **infrared (IR)** spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer.
The **Inductively coupled plasma optical emission spectroscopy (ICP-OES)** analyses were made with a Varian ICP-OES 720ES.Electrochemical/cyclic voltammetry (CV) measurements were recorded on a PAR 273 potentiostat under a nitrogen atmosphere.
Size Exclusion Chromatography (SEC) of dendrimer 2 was performed using a JASCO HPLC pump type 880-PU, TOSOHAAS TSK gel columns (G4000, G3000, G2000 with pore sizes of 20,75, and 200 Å respectively, connected in series), a Varian (series RI-3) refractive index detector, with THF as the mobile phase and calibrated with polystyrene standards.
Dynamic Light Scattering (DLS) measurements were made using a Malvern Zetasizer 3000 HSA instrument at 258C at an angle of 90°.
Elemental Analysis (EA) results were obtained using a Thermo Flash 2000 EA; the samples were introduced in a tin container for CHS analysis.
Transmission Electron Microscopy (TEM) were done by Lionel Salmon at the "Laboratoire de Chimie de Coordination" (*LCC), CNRS, 205 Route de Narbonne, 31077 Toulouse Cedex, France.*

2. G1-81 TEG 2 synthesis and characterizations



1,2,3-triazolyl G1 dendrimer with 81 TEG termini 2

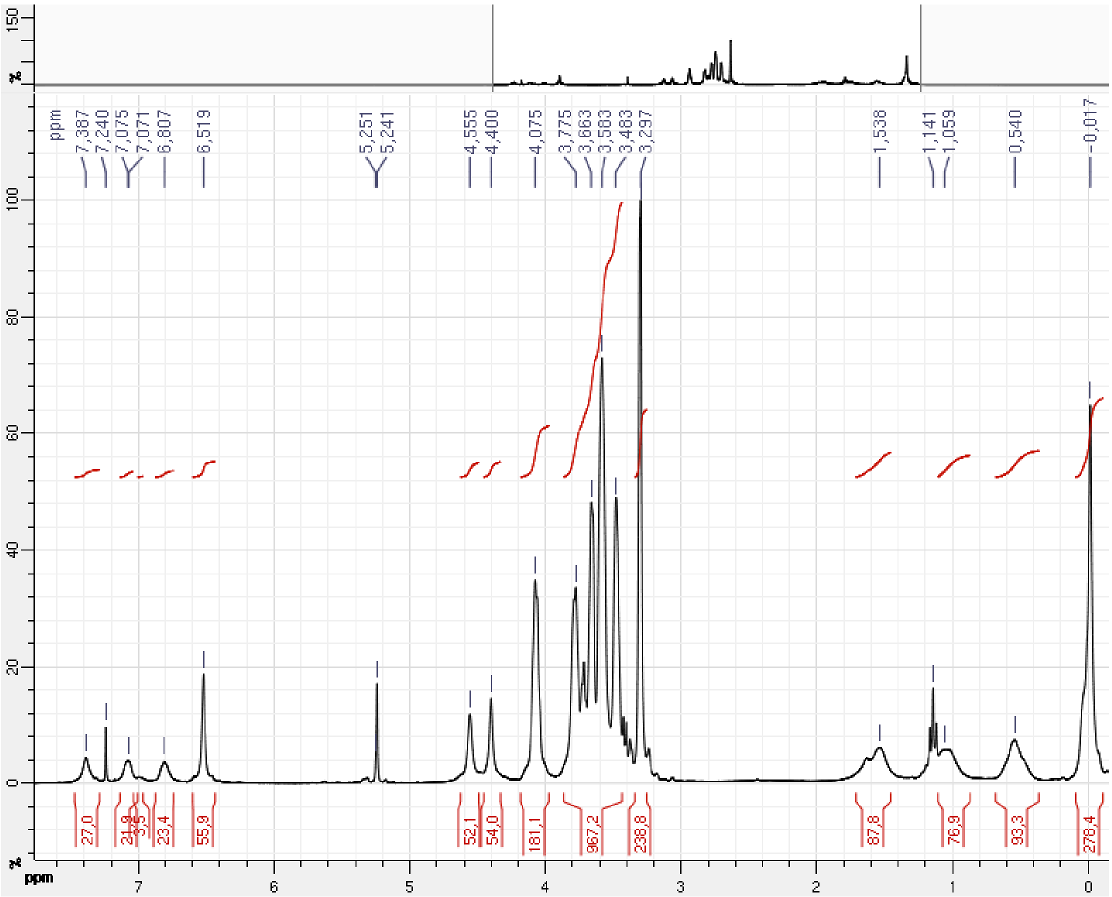
Synthesis of the dendrimer G1-81 TEG 2



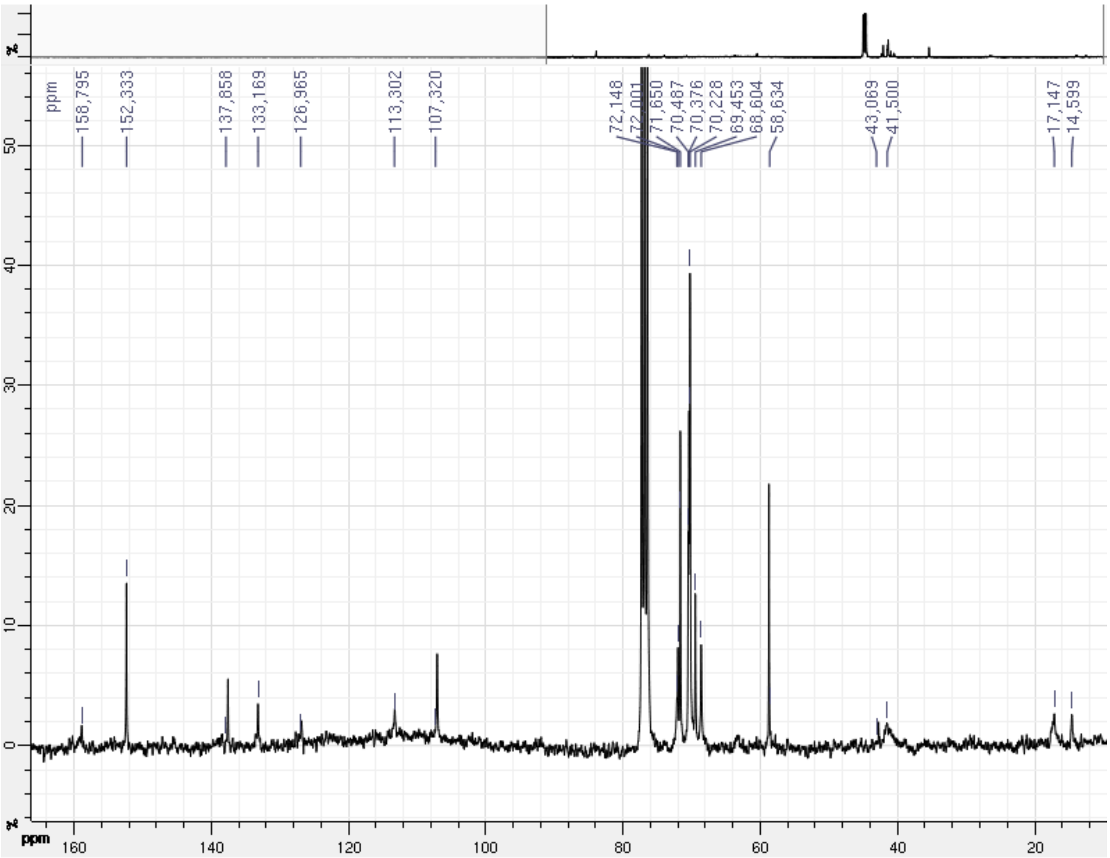
3[s1] (0.073 g, 0.012 mmol) and **4**[8] (0.199 g, 0.388 mmol, 1.2 *equiv*. *per* branch) are dissolved in THF. $CuSO_4.5H_2O$ is added (0.079 g, 0.323 mmol, 1 *equiv*. per branch, 1M in aqueous solution), followed by the dropwise addition of a freshly prepared solution of sodium ascorbate (0.125 g, 0.646 mmol, 2 *equiv*. per branch, 1M in water solution) in order to set a 1:1 THF/water ratio. The reaction mixture is stirred for 3 days at 25°C under N_2. After removing THF under vacuum, CH_2Cl_2 (100 mL) and an aqueous ammonia solution (2.0 M, 50 mL) are successively added. The mixture is allowed to stir for 10 minutes in order to remove all the Cu^{II} trapped inside the dendrimer as $[Cu(NH_3)_2(H_2O)_2]$ $[SO_4]$. The organic phase is washed twice with water, then this operation is repeated three more times to ensure the complete removal of copper ions. The organic phase is dried with sodium sulfate, and the solvent is removed under vacuum. The product is washed with 50 mL diethyl ether several times in order to remove the excess of **4**. 0.180 g of **2** is obtained (68 % yield).

Characterizations of the dendrimer G1-81 TEG 2:

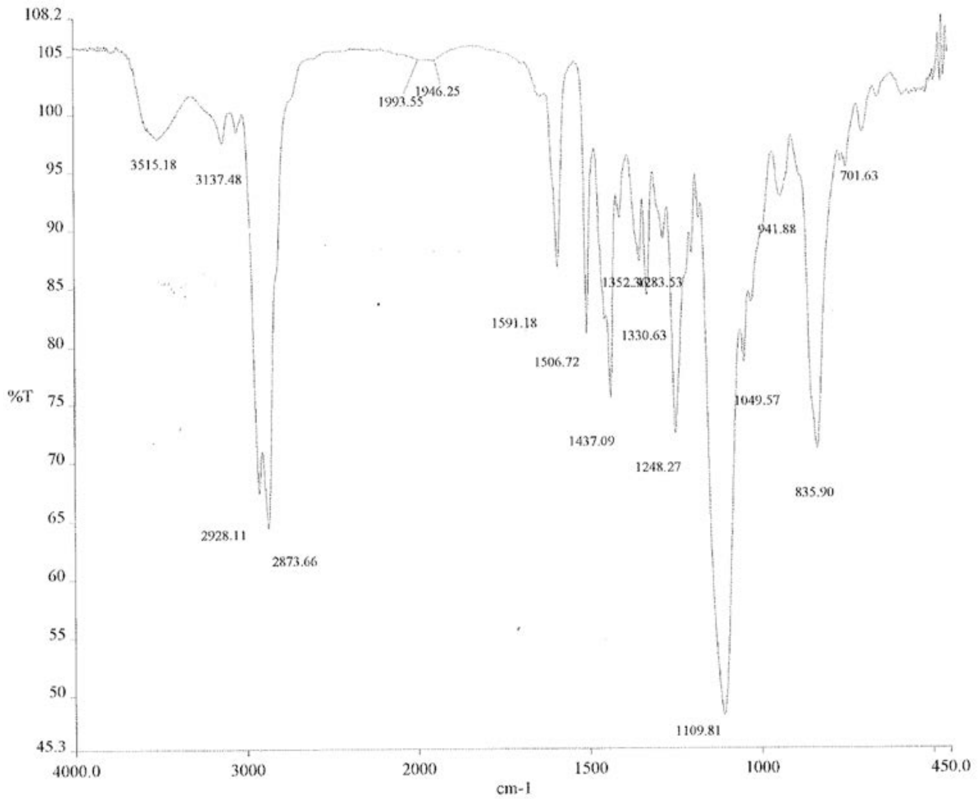
The dendrimer G1-81 TEG 2 has been characterized by ^{1}H NMR, ^{13}C NMR, IR, UV-Vis., SEC, EA, NMR DOSY, ICP-OES. These data are detailed below.



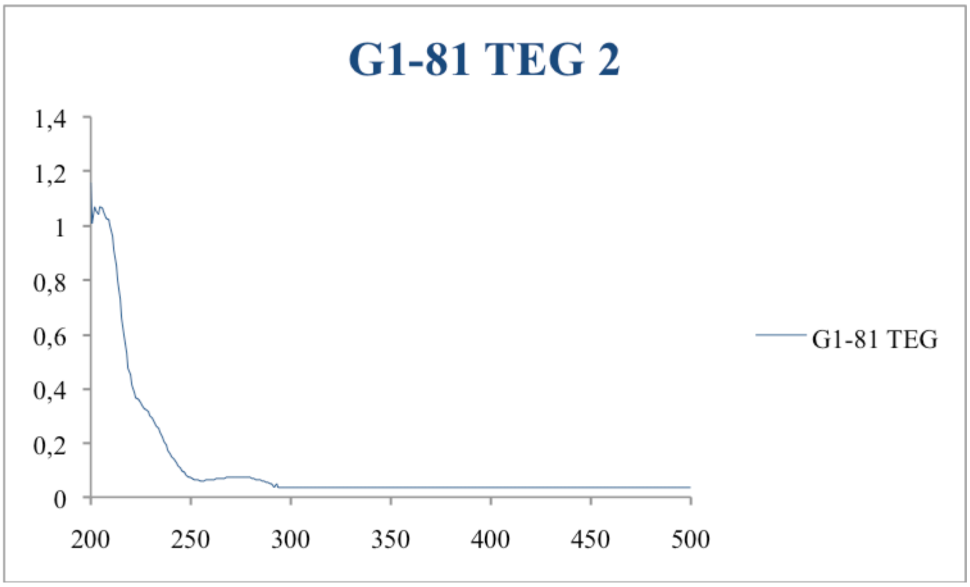
^{1}H NMR spectrum of **2** ($CDCl_3$, 300 MHz) δppm: 7.38 (CH-triazole), 7.075 (CH-arom. in middle), 7.071 (CH-arom. intern.), 6.80 (CH-arom. in middle), 6.51 (CH- arom. extern.), 4.55 (triazole-CH_2-0), 4.40 (O-CH_2-arom. extern.), 4.07 (CH_2O-arom. extern. and Si-CH_2-triazole), 3.77-3.48 (OCH_2CH_2O), 3.29 (CH_3O), 1.53 ($CH_2CH_2CH_2Si$), 1.05 ($CH_2CH_2CH_2Si$), 0.54 ($CH_2CH_2CH_2Si$), 0.01 ($Si(CH_3)_2$).



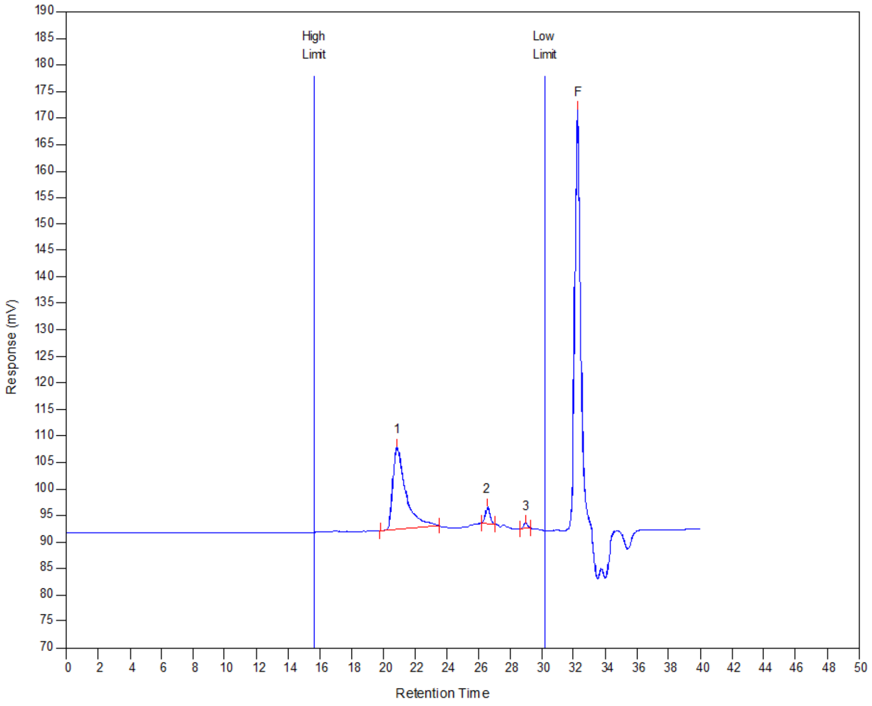
<u>^{13}C NMR spectrum of **2**</u> ($CDCl_3$, 300 MHz) δppm: 158.7 (Cq-O arom. intern), 152.3 (*C*q-O arom. extern.), 137.8 (*C*q-CH_2 arom.), 133.1 (Cq-*C*H_2-O), 126.9 (arom. core), 113,3 (CH arom. intermediate) 107.0 (*C*H arom.), 70.4 (O*C*H_2*C*H_2O), 58.6 (*C*H_3O), 43.0 (*C*$H_2CH_2CH_2$Si), 41.5 (SiC*H*$_2$-triazole), 17.1 (CH_2*C*H_2CH_2Si), 14.6 (CH_2CH_2*C*H_2Si), (-4.1 (Si(*C*H_3)$_2$) normaly). All the peaks are in accord with G1-81 TEG **2**, and quite similarly to G0-27 **1**[46].



IR spectrum of **2**: there is no N_3 bond at 2100 cm^{-1}, which indicates that the “click” reaction is completed. The spectrum is similar to the IR spectrum of **1**[46].



UV-vis. spectrum of **2**. The UV-vis. spectra have been recovered with water as blank. The concentration of G1-81 TEG **2** is 1.33 nM.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6405	5291	5656	5947	6179	5608	1.06899
2	638	634	635	637	638	635	1.00158
3	260	261	261	261	262	260	1
4	0	0	0	0	0	0	0

Size extrusion chromatogram: SEC of G1-81 TEG **2**. Peak n°1 corresponds to **2,** its polydispersity is 1.07. The reference used is linear polystyrene.

Determination of the dendrimer radius in solution using the diffusion coefficient determined by ^{1}H NMR:

A ^{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 diffusion coefficient D of the molecules in solution that gives access the hydrodynamic radius.

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

Stokes-Einstein law: D = KBT / 6лηrH

D: diffusion constant; KB: Boltzman's constant; T: temperature (K); η: solvent viscosity; rH: hydrodynamic radius of the species.

DOSY: $D = 5.8\ (\pm 0.1) \times 10^{-11} m^2/s$

$K_B = 1.38 \times 10^{-23}\ m^2.kg.s^{-2}.K^{-1}$

$T = 298\ K$

$\eta = 0.57 \times 10^{-3}\ Pa.s$

→ $r_H = K_BT/6л\eta D = 6.6\ (\pm 0.1)\ nm$

→ Hydrodynamic diameter of **2**: 13.2 (± 0.2) nm

The mass spectrum could not be obtained, because of the huge weight of G1-81 TEG **2**.

Elemental analysis

Experimental results

C: 57.8%

N: 4.8%

H: 8.3%

theoretical results

C: 57.8%

N: 4.8%

H: 8.4%

Inductively coupled plasma optical emission spectroscopy (ICP-OES):

25.9 mg of **1** are dissolved in 4 mL of water (volume necessary for the analysis). The ICP-OES shows that all the copper has been removed (Cu quantity < 0.1 ppm which is the detection limit of the apparatus**).** The same analysis for **2** has been carried out.

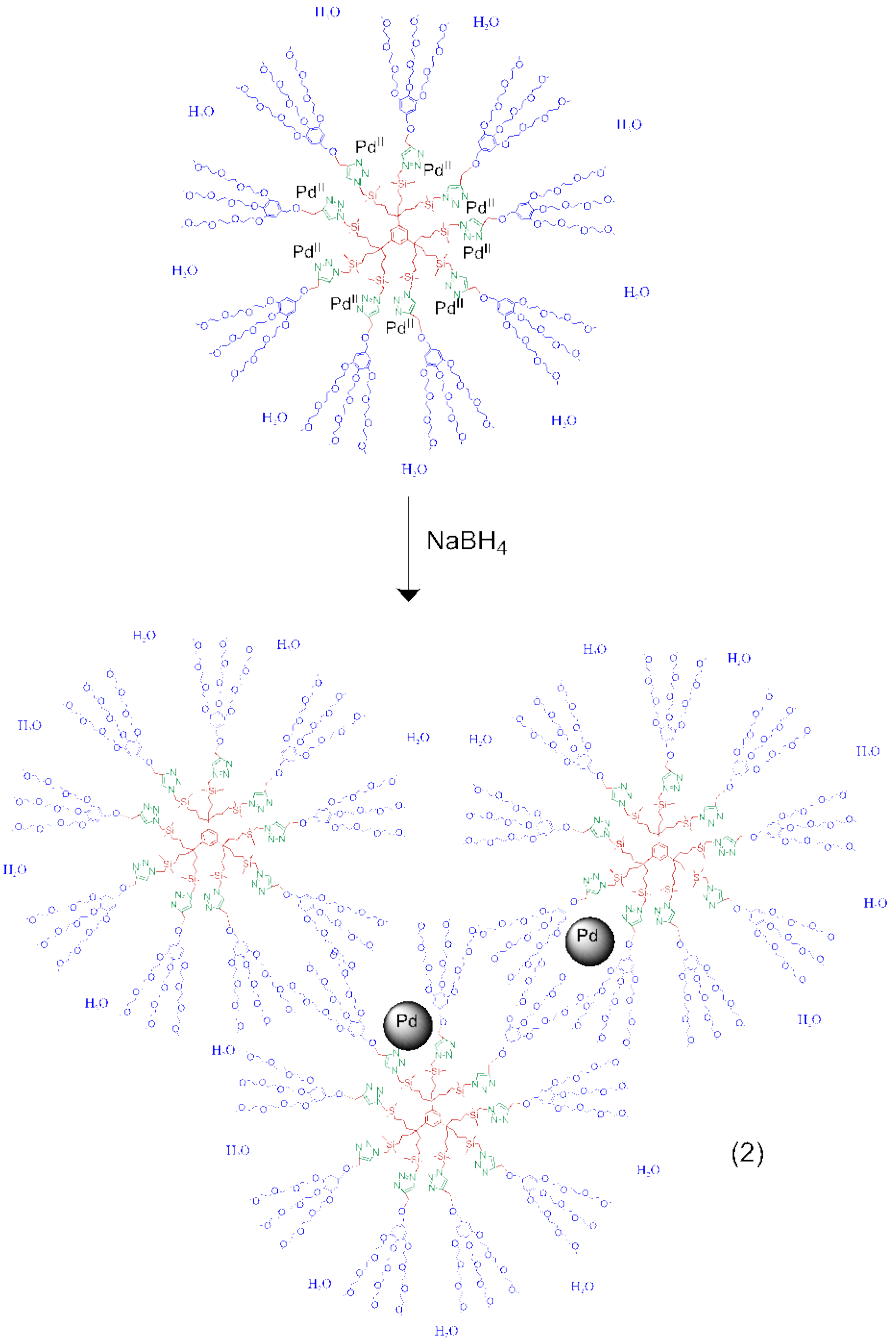
3. PdNP synthesis

Preparation of the PdNPs for catalysis

3.6×10^{-4} mmol of dendrimer **1** (2.59 mg) is dissolved in 1.1 mL of water in a Schlenk flask, and an orange solution of K_2PdCl_4 (3.2×10^{-3} mmol in 1.1 mL water) is added to the solution of the dendrimer. 30 mL of water is added, and the solution is stirred for 5 min. The concentration of Pd^{II} is 0.1 mM. A 1 mL aqueous solution containing 3.2×10^{-2} mmol of $NaBH_4$ is added dropwise, provoking the formation of a brown/black color (see below) corresponding to the reduction of Pd^{II} to Pd^0 and PdNP formation.

Figure S1: Preparation of the PdNPs.

Then, dialysis is conducted for 1 day in order to remove excess $NaBH_4$ and eventually purify the PdNPs from any Pd derivatives. Thereafter, ICP-OES analysis indicates that the Pd loading in the PdNPs solution is 96% of starting Pd. This solution is directly used for catalysis. 10 mL of this solution are used when 0.1 mol % Pd per mol substrate is needed for a reaction between 1 mmol of halogenoarene and 1.5 mmol of boronic acid, and 10 µL of this solution are used when 1 ppm Pd per mol substrate is needed.



(2)

The average number of Pd atoms in the G0-TEG-dendrimer **1** PdNPs is around 100 (with a large proportion on edges and corners) and that for G1-TEG **2** PdNPs is around 1000. Thus, although there are only 9 Pd^{II} per G0-TEG dendrimer **1** and 27 Pd^{II} per G1-TEG dendrimer **2**, the number of Pd atoms in the dendrimer-stabilized PdNPs are considerably larger than the number of Pd^{II} ion precursor in each dendrimer. This means that the large majority of dendrimer molecules do not contain a PdNP, and there is thus interdendritic contribution to the strong PdNP stabilization, specifically with **1** that has a relatively small size. That several dendrimers (11 small G0-TEG dendrimers **1**) are necessary to stabilize a single PdNP is a situation that is in sharp contrast to the one previously encountered with ferrocenyl-terminated click dendrimers for which the number of Pd atoms in the PdNP matched that of Pd^{II} precursors in each dendrimer.[6h] This contrast is due to the TEG termini of the present "click" dendrimer family.

4. Suzuki-Miyaura reaction experiments

General procedure for the catalysis of the Suzuki-Miyaura reaction

Miyaura-Suzuki reactions. In a Schlenk flask containing tribasic potassium phosphate (2 equiv.), phenylboronic acid (1.5 equiv.), aryl halide (1 equiv.) and 10 mL of EtOH (volume ratio of H_2O/EtOH: 1/1) are successively added. Then the solution containing the dendrimer-stabilized PdNPs is added. The suspension is allowed to stir under N_2 or air (no yield difference). After the reaction time (see Tables 1 and 2 of the main text), the reaction mixture is extracted twice with diethyl ether (Et_2O, all the reactants and final products are soluble in Et_2O), the organic phase is dried over Na_2SO_4, and the solvent is removed under vacuum. In parallel, the reaction is checked using TLC in only petroleum ether as eluent in nearly all the cases (see below), and ^1H NMR. Purification by flash chromatography column is conducted with silica gel as stationary phase and petroleum ether as mobile phase (see below). Another procedure of purification consists in cooling the Schlenk flask at the end of the reaction. The product precipitates, and a simple filtration allows to obtain the product that is then washed with a cold solution of H_2O/EtOH. After each reaction, the Schlenk flask is washed with a solution of aqua regea (3 volumes of hydrochloric acid for 1 volume of nitric acid) in order to remove traces of Pd. The Suzuki-Miyaura reactions with G0-PdNPs between phenylboronic acid and 1,4-chloronitrobenzene is best conducted under the above conditions using KOH as a base. During the investigation of the Suzuki-Miyaura coupling with bromoarenes, the formation of some Pd black is observed on the wall of the vessel several hours after the reaction, but only at 80°C (when the quantity of Pd used is sufficient to be observable). The yield of the reaction after 1 day (entry 28 or 36 of the main text **table 2**) is enhanced, however, by continuing the reaction one more day (respectively entries 29 and 37). It means that 0.01 mol % of Pd is still active after 1 day at 80°C. Attempts to carry out reactions for more than 3 days at 80°, however, do not improve the yield, which is an evidence of inactivity after that time. The yield of the reaction with 1 ppm (and 0.3 ppm) is also improved after 1 day and until 2.5 days.

Study of the substrate concentration during the Suzuki-Miyaura reaction

The synthesis of PdNPs following this method brings a 33 ml water solution of PdNPs. When 0.1% mol Pd is used for a reaction containing 1 mmol of aryl halide, 10 mL of this PdNPs solution are used (and 10 mL ethanol added at same time). In this case, the concentration of substrate is limited to 20 mL of solvent by 1 mmol of aryl halide i.e. 0.05 $mol.L^{-1}$. When less catalyst is used, one must make sure that enough solvent is used in order to stir the mixture because in some cases the base, the halide, and the phenyl boronic acid are solid. The Suzuki-Miyaura reaction between the 1,4-bromonitrobenzene and the phenyl boronic acid has been carried out in various volumes of H_2O/EtOH (1/1) with 0.001% of PdNPs at 80°C during 36h. When less solvent is used, the catalysis seems to work better (table S1).

Table S1. Study of substrate concentration in the reaction.

entry	Total volume (mL)	Concentration of halide (mol.L^{-1})	Yield (%)
46	40	0.025	58
37	20	0.05	98
47	10	0.1	99
48	5	0.2	99

Each reaction has been carried out with 1 mmol of aryl halide, 1.5 mmol of aryl boronic acid and 2 equiv. K_3PO_4 in EtOH/H_2O (1/1).

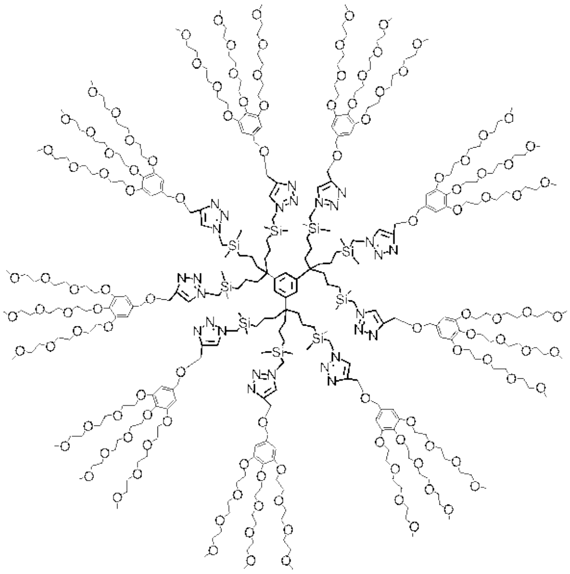
Study of homocoupling

Homocoupling between two iodobenzene molecules, i.e. Ulmann-type coupling, is also catalyzed by the G0-PdNP, and at 28°C it does not occur in the absence of PdNPs. With 0.1 mol % of these efficient PdNPs, the homocoupling yield is 20% in 24 h at 28°C, but lower amounts of G0-PdNPs give 0% yield of biphenyl, the homocoupling product, whereas a quantitative Suzuki-Miyaura coupling yield is obtained with iodobenzene and phenyl acid boronic in 24h with 10 ppm of Pd. In the absence of iodoarene, no biphenyl is produced either in the presence of phenylboronic acid with 0.1% G0-PdNPs. This shows that the G0-PdNP-catalyzed cross-coupling reaction of iodobenzene occurs with complete selectivity.

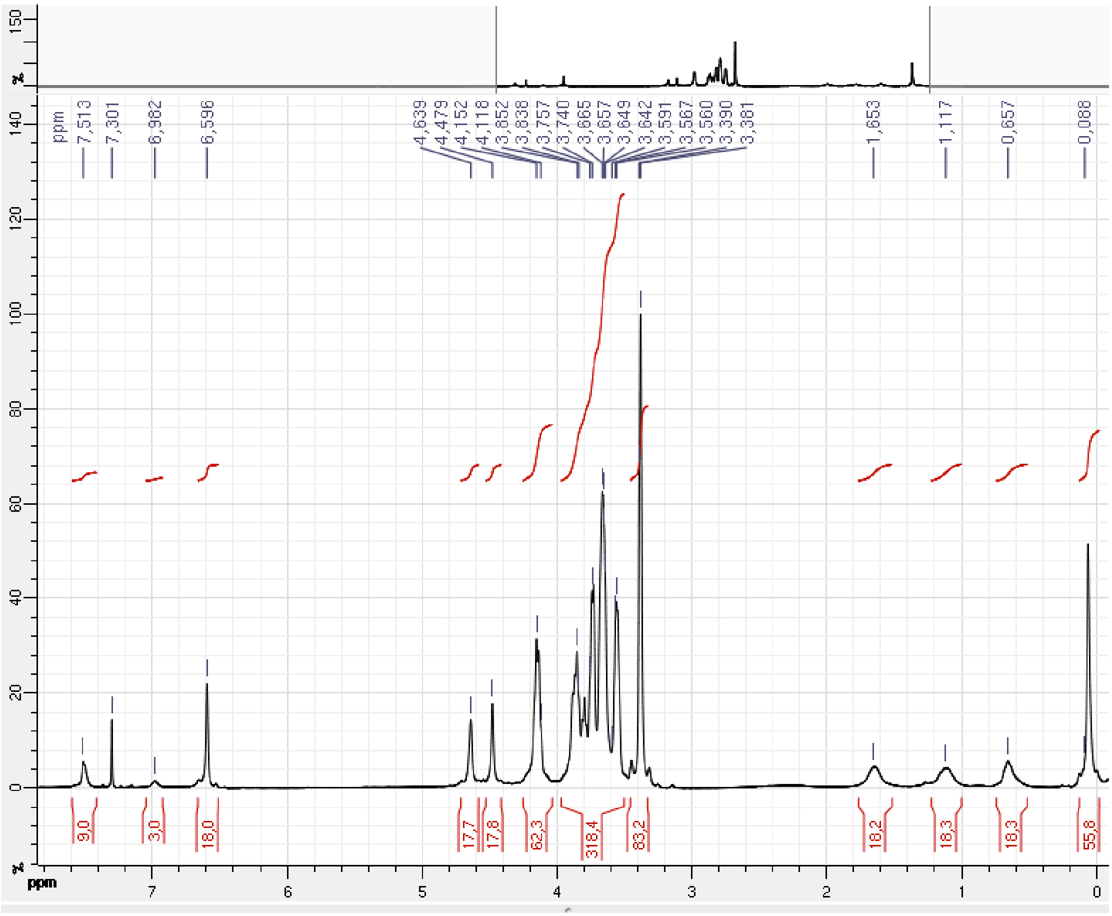
Recovery of the dendrimers[8]

After the extraction of products by Et_2O from the aqueous phase, the dendrimer (insoluble in Et_2O) is extracted with dichloromethane.

5. NMR spectra

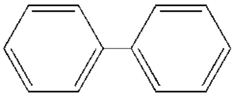


1,2,3-triazolyl G0 dendrimer with 27 TEG termini 1

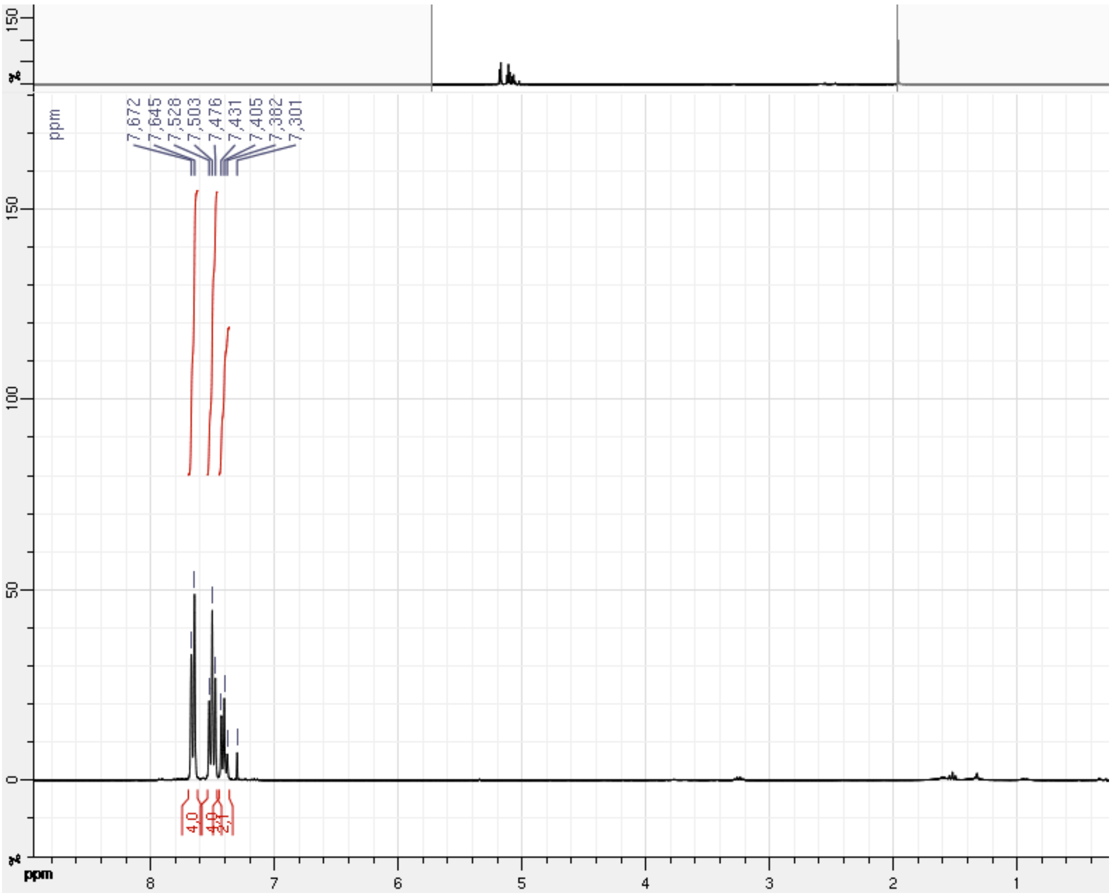


^{1}H NMR spectrum of **1** [9c] (CDCl$_3$, 300 MHz) δppm: 7.51 (C*H*-triazole), 6.98 (CH-arom. intern.), 6.59 (CH- arom. extern.), 4.64 (triazole-CH$_2$-0), 4.47 (O-CH$_2$-arom. extern.), 4.15-4.11 (CH$_2$O-arom. extern. and Si-CH$_2$-triazole), 3.56-3.85 (OCH$_2$CH$_2$O), 3.38-3.39 (CH$_3$O), 1.65 (C*H*$_2$CH$_2$CH$_2$Si), 1.11 (CH$_2$CH$_2$CH$_2$Si), 0.65 (CH$_2$CH$_2$CH$_2$Si), 0.08 (Si(CH$_3$)$_2$).

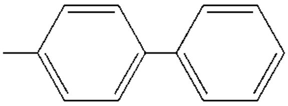
^{1}H NMR for the products of the Suzuki-Miyaura reactions



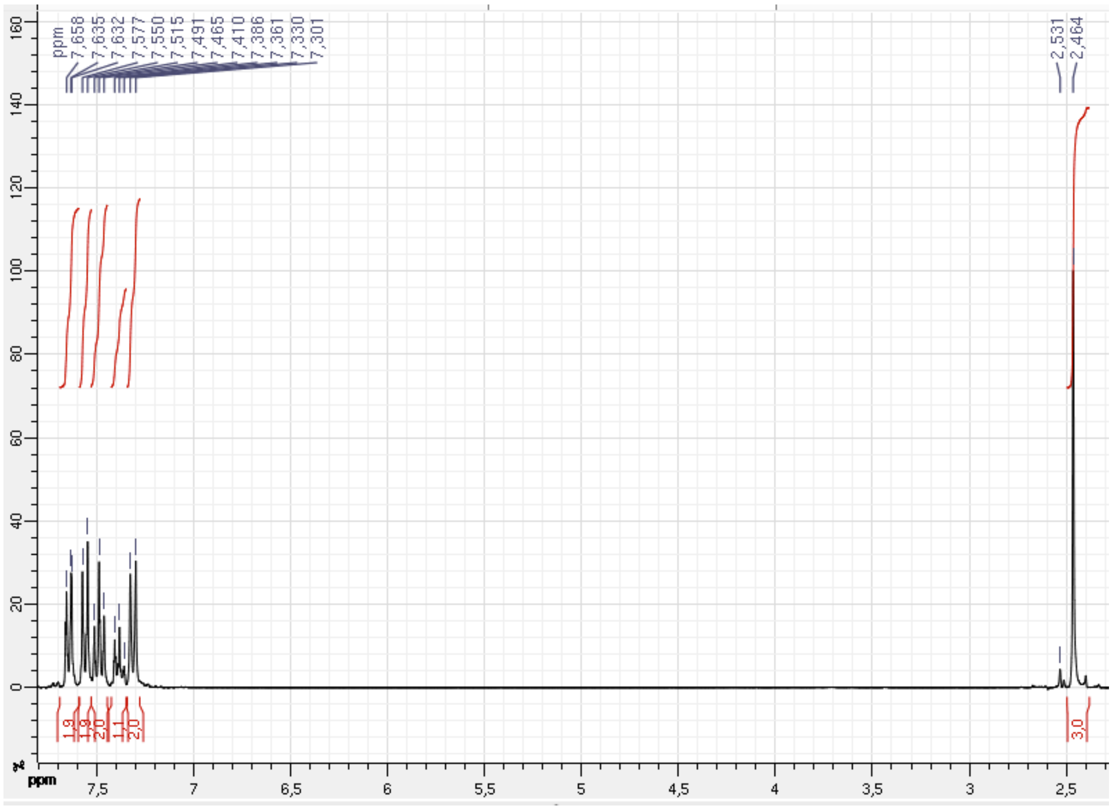
biphenyl



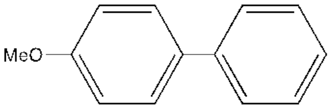
^{1}H NMR spectrum of biphenyl ($CDCl_3$, 300 MHz) δppm: 7.38-7.43 (t, 2H), 7.47-7.52 (m, 4H), 7.64-7.67 (d, 4H).



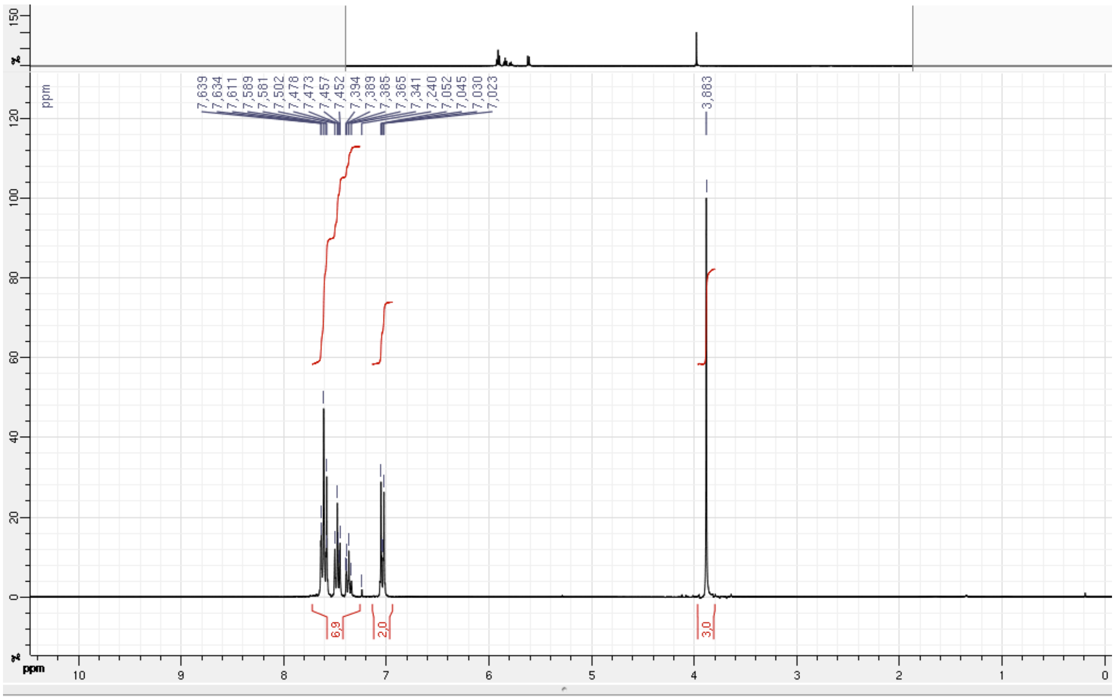
4-methylbiphenyl



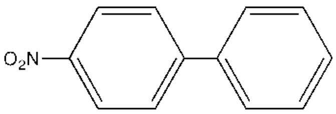
^{1}H NMR spectrum of 4-methylbiphenyl: (CDCl$_3$, 300 MHz) δppm: 2.48 (S, CH$_3$-arom. 3H), 7.30-7.33 (d, 2H), 7.36-7.41 (m, 1H) 7.46-7.51 (t, 2H), 7.55-7.57 (d, 2H), 7.63-7.65 (q, 2H).



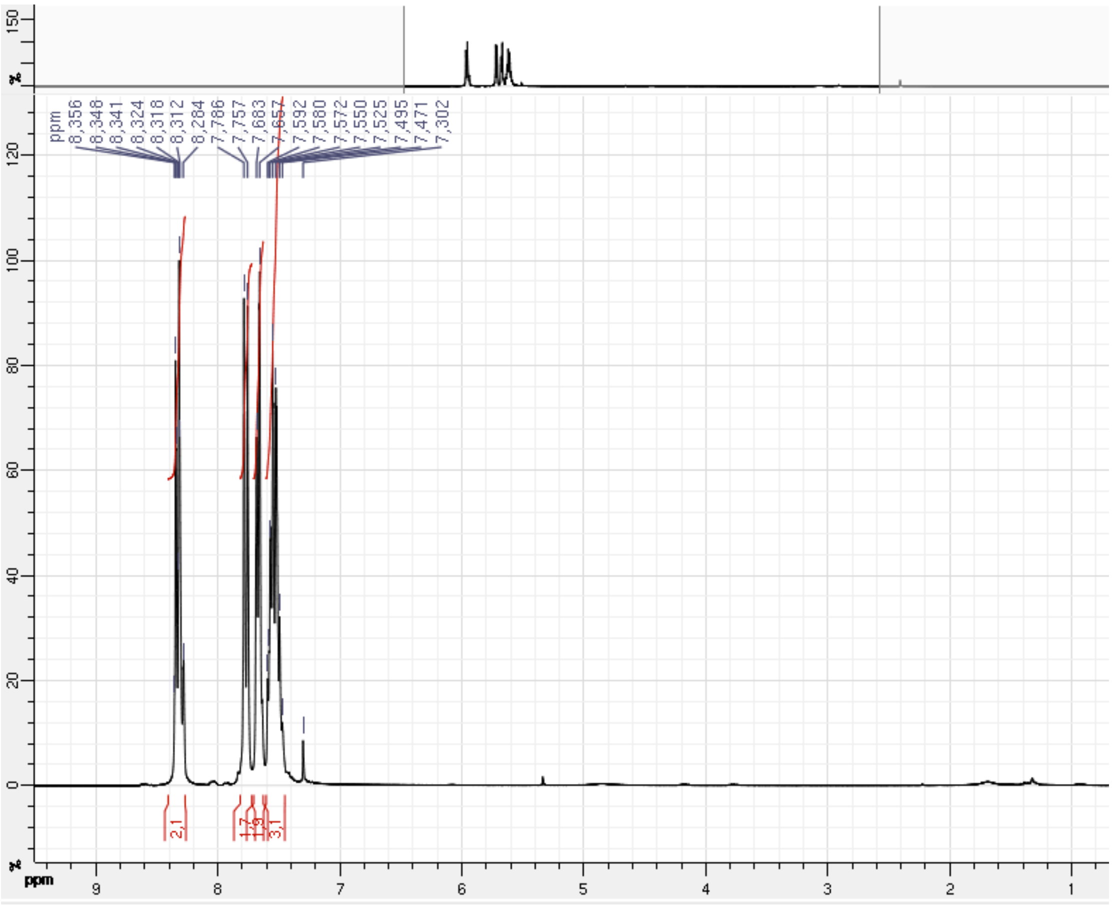
4-methoxybiphenyl



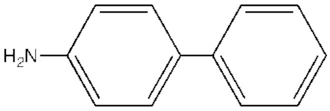
^{1}H NMR spectrum of 4-methoxybiphenyl**:** (CDCl$_3$, 300 MHz) δppm: 2.88 (S, CH$_3$O-arom. 3H), 7.02-7.05 (d, , 2H), 7.34-7.39 (m, 1H) 7.45-7.50 (m, 2H), 7.58-7.63 (m, 4H).



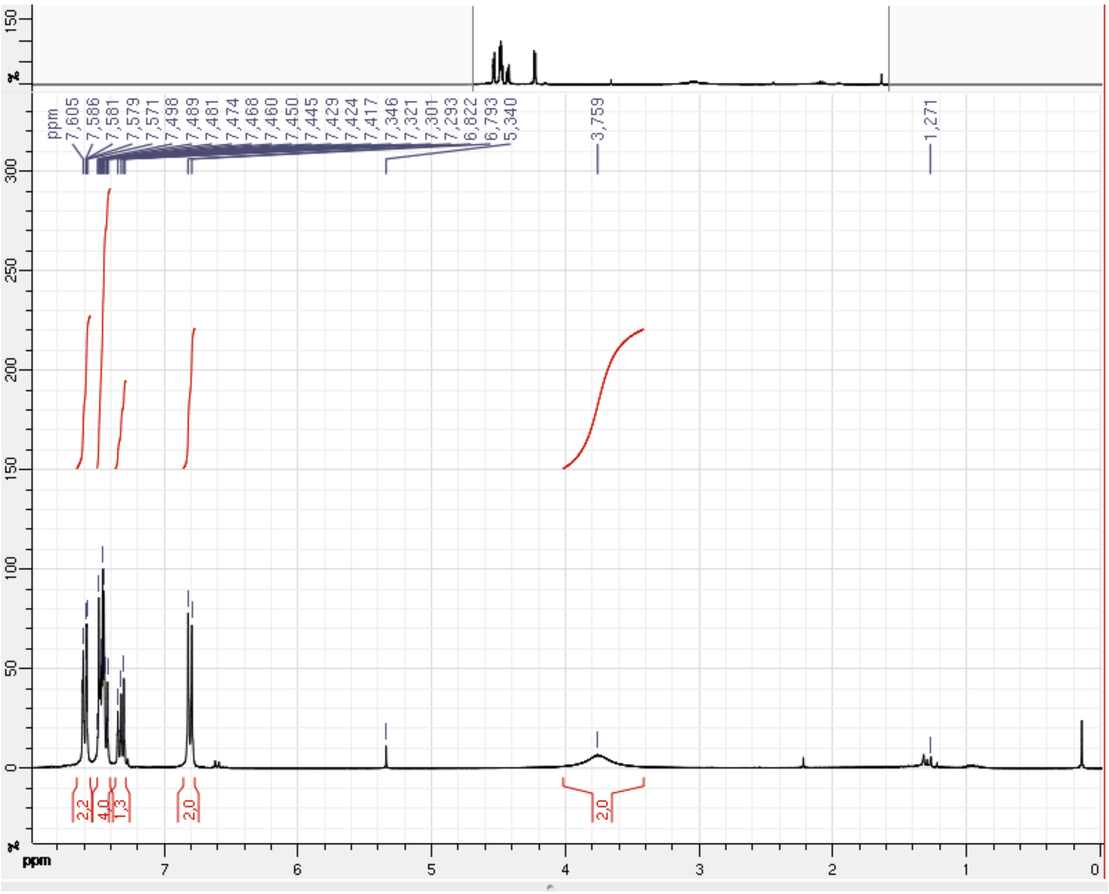
4-nitrobiphenyl



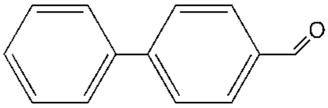
^{1}H NMR spectrum of 4-nitrobiphenyl: *^{1}H NMR* ($CDCl_3$, 300 MHz) δppm: 7.47-7.59 (2m, 1H, 2H), 7.65-7.68 (d, 2H) 7.75-7.78 (d, 2H), 8.29-8.35 (d, 2H).



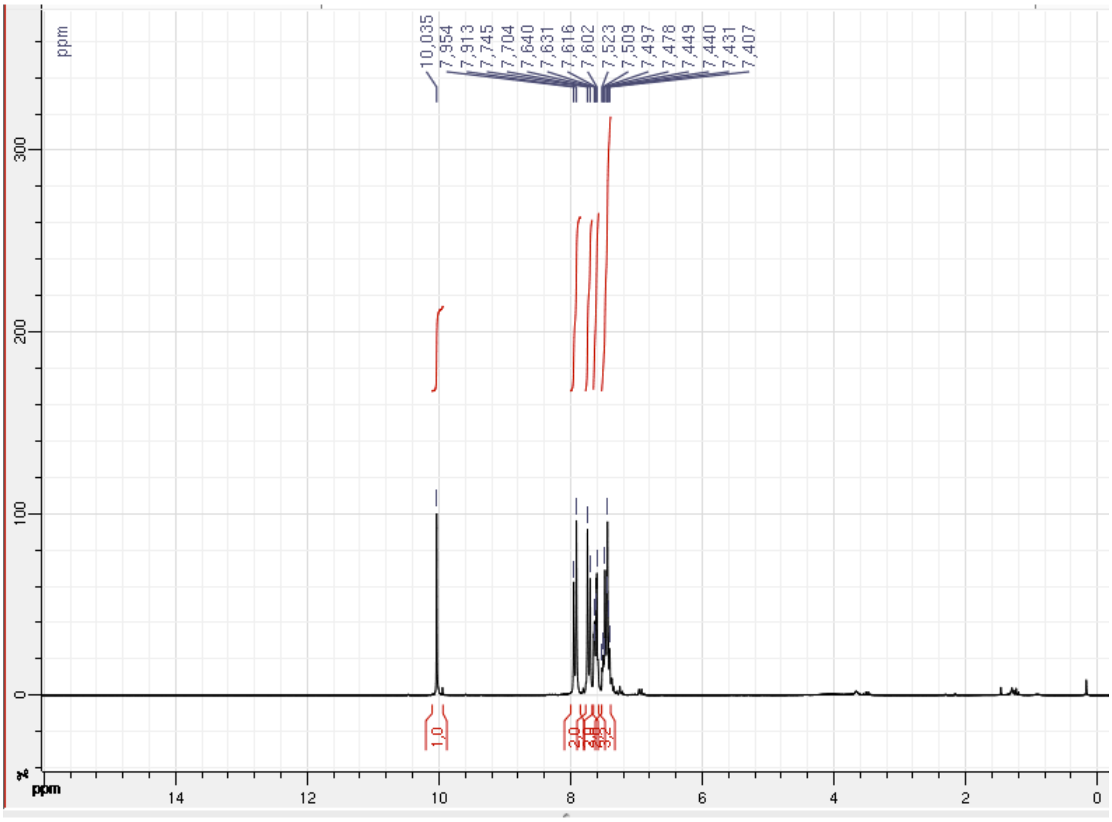
4-aminobiphenyl



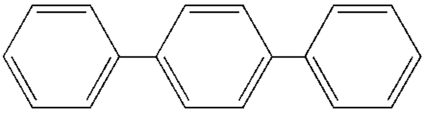
^{1}H NMR spectrum of 4-aminobiphenyl: ($CDCl_3$, 300 MHz) δppm: 6.79-6.82 (d, 2H), 7.29-7.34 (m, 1H) 7.41-7.49 (2m, 4H), 7.57-7.60 (d, 2H).



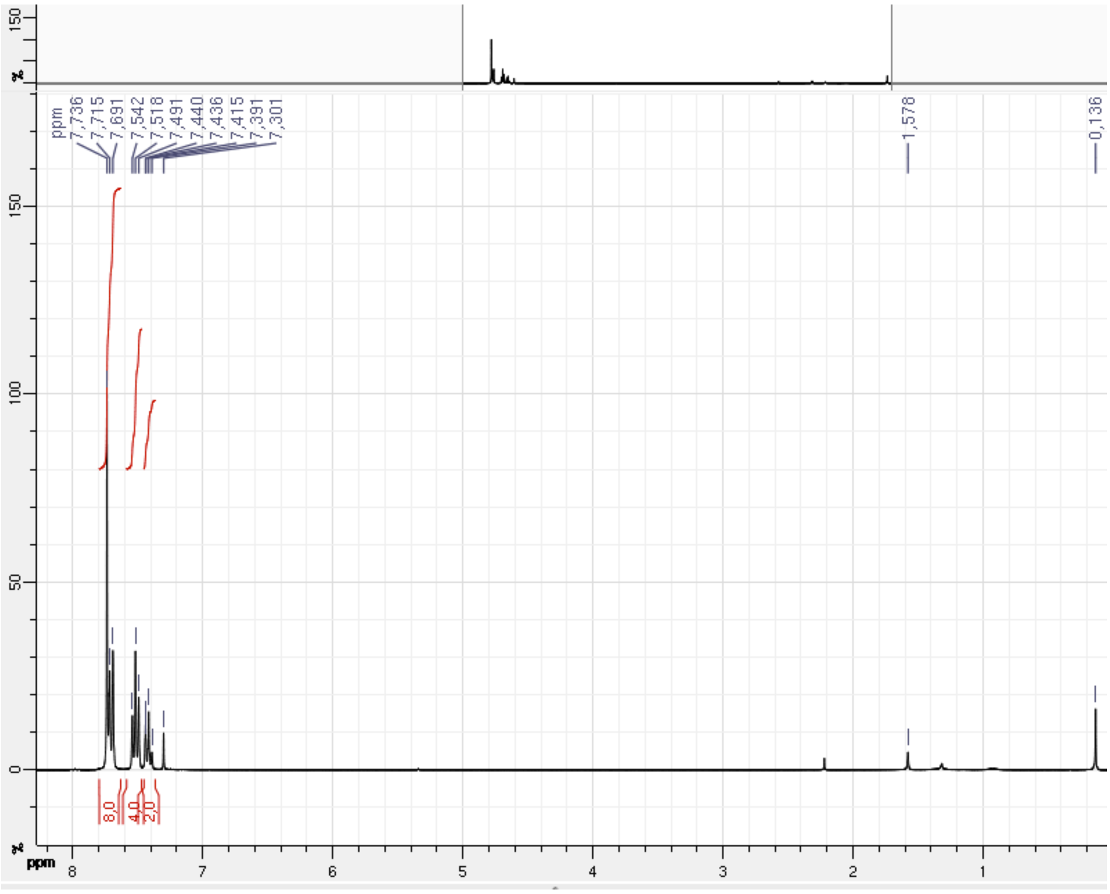
biphenyl-4-carboxaldehyde



^{1}H NMR spectrum of biphenyl-4-carboxaldehyde: ($CDCl_3$, 300 MHz) δppm: 7.40-7.52 (d + s, 2H + 1H), 7.60-7.64 (d, 2H), 7.70-7.45 (d, 2H), 7.91-7.95 (d, 2H), 10.03 (s, 1H aldehyde).



Terphenyl



^{1}H NMR spectrum of terphenyl: ($CDCl_3$, 300 MHz) δppm: 7.39-7.44 (m, 2H), 7.49-7.54 (m, 4H) 7.69-7.73 (m, 8H).

<u>6. PdNPs-dendrimer and Pd^{II}-dendrimer characterizations</u>

PdNPs and Pd^{II} interactions with the dendrimer have been analyzed by TEM, HRTEM, EDX, DLS, UV-vis., and ^{1}H NMR.

<u>Transition Electron Microscopy (TEM) data of PdNPs stabilized by G0-27-TEG and G1-81 TEG.</u>

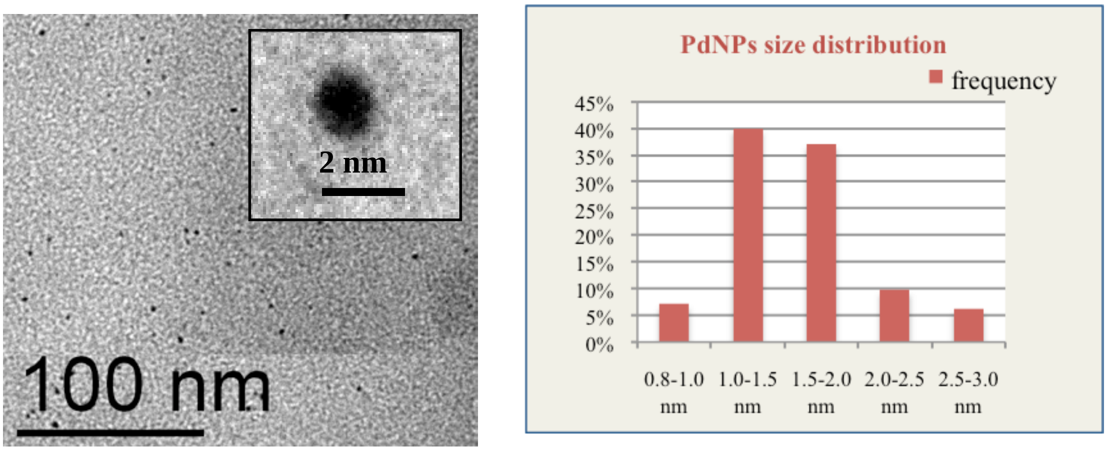


Figure S2: TEM analysis of PdNPs stabilized by G0-27 TEG, **1,** (left) and their size dispersity (right); average value: 1.4 ± 0.7 nm.

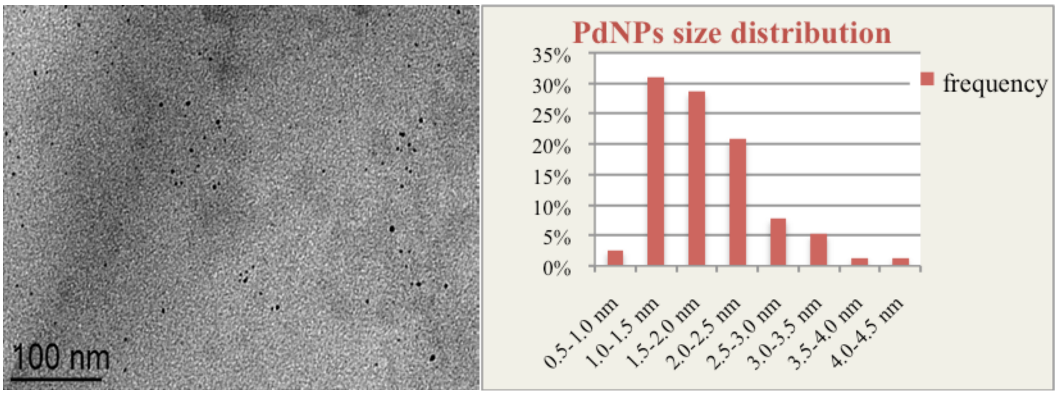


Figure S3: TEM analysis of PdNPs stabilized by G0-27 TEG, **1,** (left) after 2 months of air exposition and their size dispersity on 145 PdNPs (right) average value: 1.5 ± 0.7 nm.

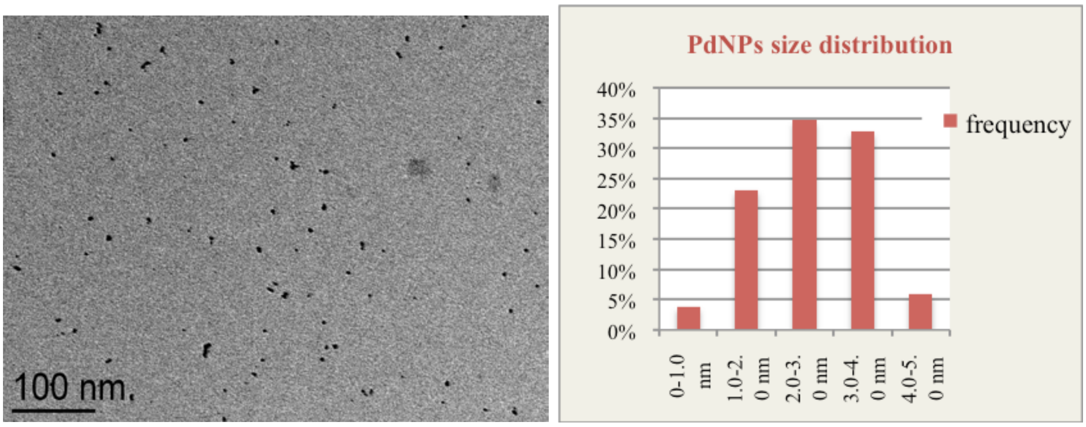


Figure S4: TEM analysis of PdNPs with 1 eq of Pd^{II} per triazole stabilized by G1-81 TEG, **2**, (left) and their size dispersity on 100 PdNPs (right), average value: 2.7 ± 1 nm.

High Resolution Transition Electron Microscopy (HRTEM) and Energy-Dispersed Spectroscopy data of PdNPs stabilized by G0-27-TEG.

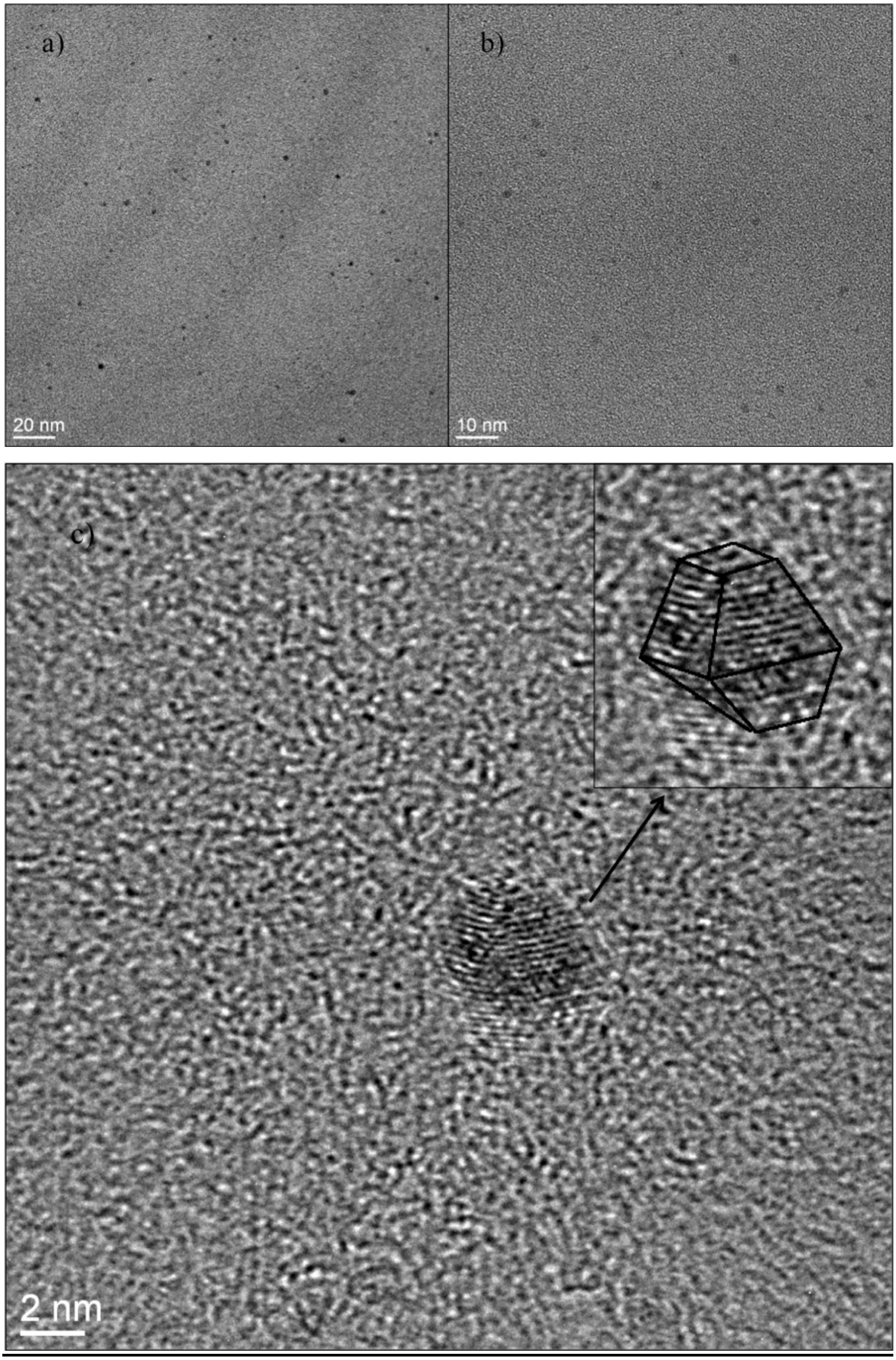

a)
20 nm
b)
10 nm
c)
2 nm

Figure S5: HRTEM analysis of PdNPs with 1 eq of Pd^{II} per triazole stabilized by G0-27 TEG, 1. a),b) HRTEM of PdNPs with a zoom x100 000 and a zoom x200 000 respectively. c) crystalline mail of a PdNP. It appears that the PdNP is present under a shape of truncated bipyramid (Square bifrustum).

The Energy-Dispersed Spectroscopy has been carried out, and shows that the NPs analysed in HRTEM are PdNPs.

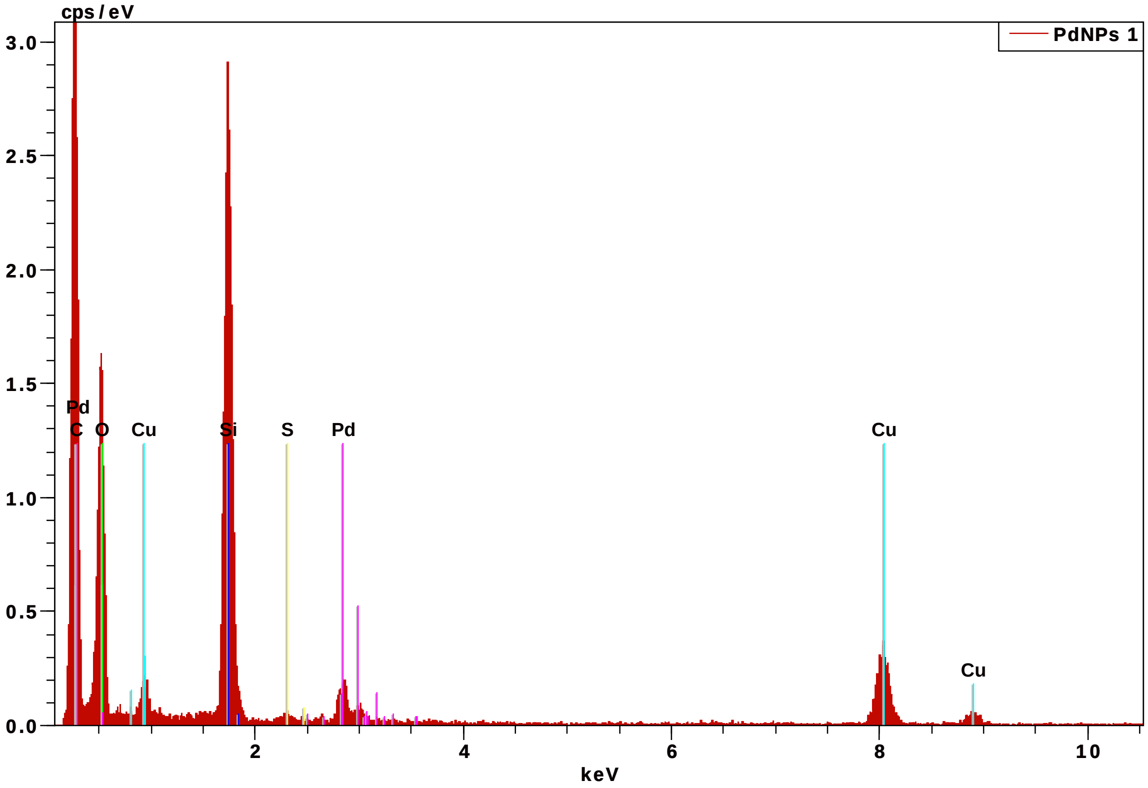


Figure S6: EDX analysis of PdNPs with 1 eq of Pd^{II} per triazole stabilized by G0-27 TEG, 1.

Dynamic light scattering analyses

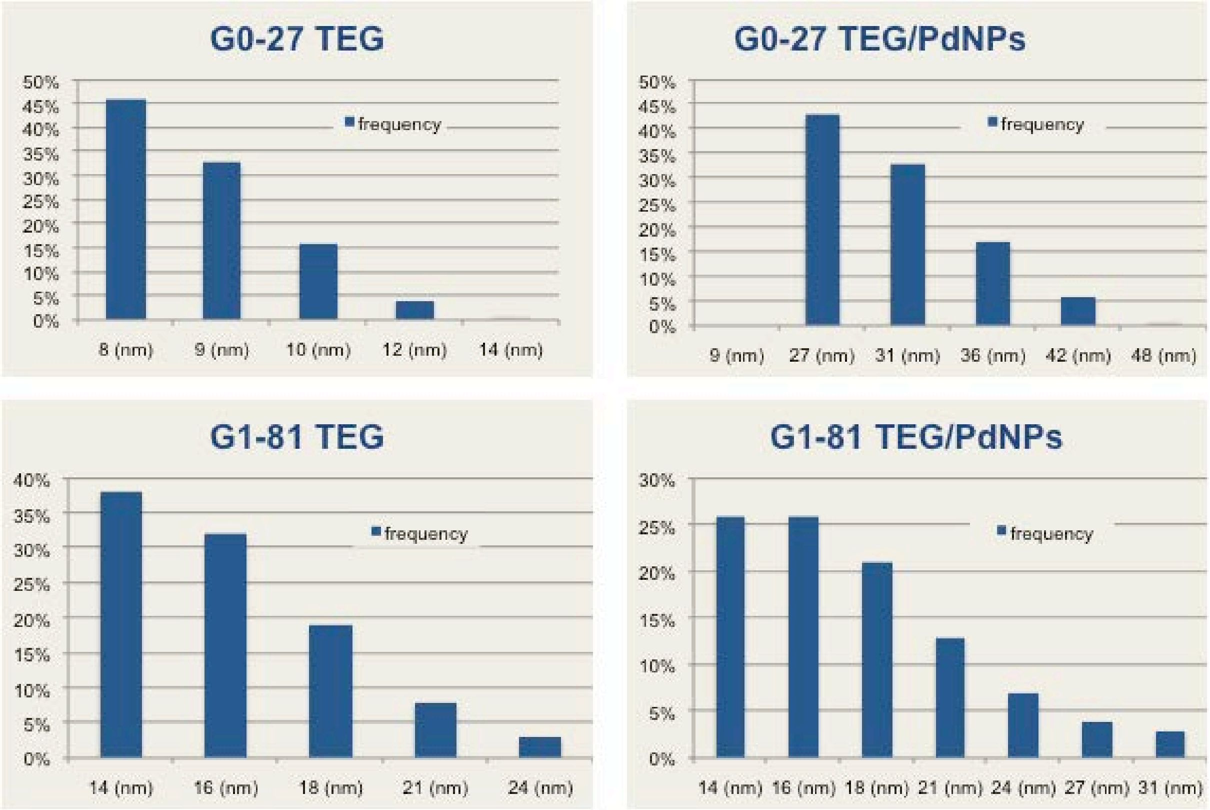
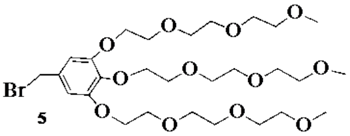


Figure S7: Dynamic Light Scattering (DLS) of dendrimers alone and dendrimers assemblies in the presence of PdNPs. a) DLS distribution of G0-27 TEG, 1, alone. The average DLS size is 9 nm. b) DLS distribution of G0-27 TEG, 1, with PdNPs. The average DLS size is 31 nm, no assemblage has been observed before 27 nm. c) DLS distribution of G1-81 TEG, 2, alone. The average DLS size is 16 nm. d) DLS distribution of G1-81 TEG, 2, with PdNPs. The average DLS size is 18 nm.

DLS measurements have been carried out in the same water solution that those used for catalysis. The G0-27 TEG and G1-81 TEG DLS have been measured in a water solution with a concentration in dendrimer of 1.1 x10^{-2} mmol.L^{-1}. The G0-27 TEG/PdNPs and G1-81 TEG/PdNPs DLS have been measured in a water solution with a concentration in dendrimer/PdNPs of 1.1/9.7 x10^{-2} mmol.L^{-1}.

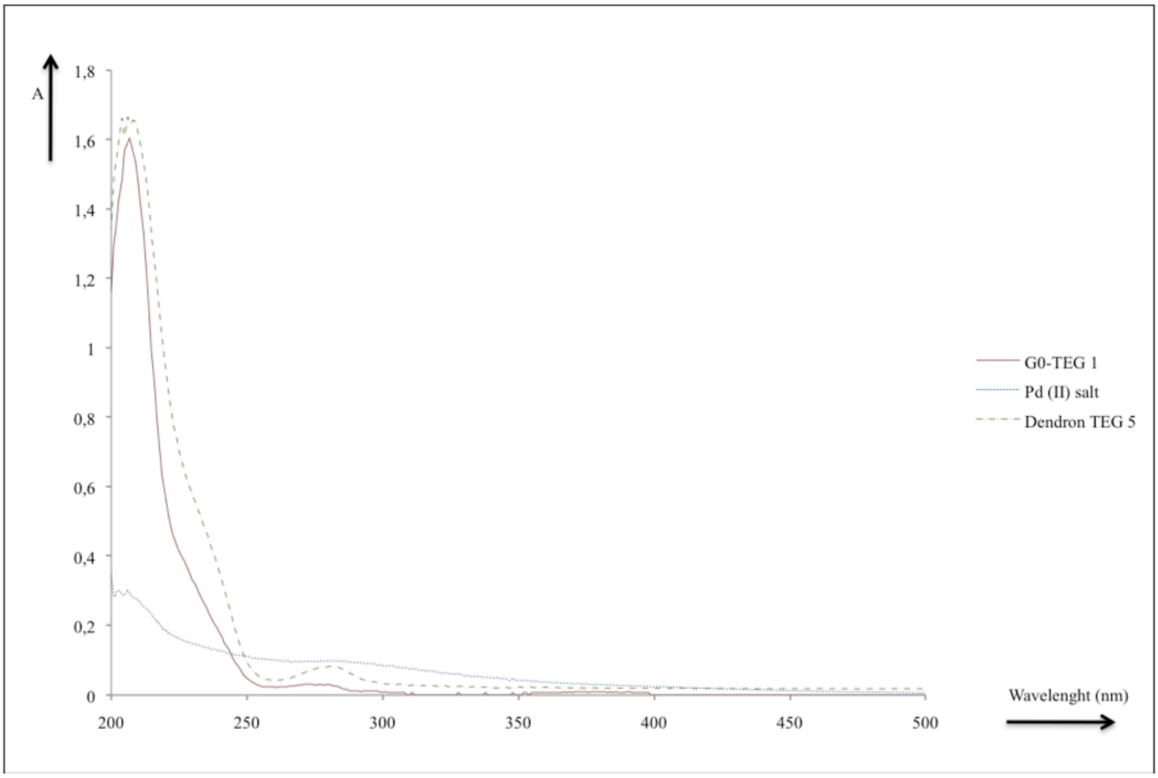
UV-vis. Spectra

Preparation of the PdNPs for UV-vis. spectroscopy



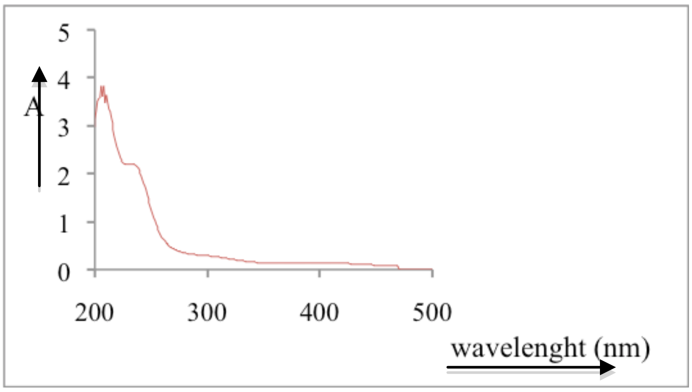
Dendron **5** has been used during the UV-vis. Studies in order to visualized the complexation of Pd^{II} with dendrimer G0-27 TEG **1**. The presence of bromine termini instead of alcohol, has been chosen in order to avoid hydrogen bonds.

The following aqueous solutions are prepared: (A) K_2PdCl_4 (c = 33 µM), (B) dendrimer **1** (c = 3.6 µM) and (C) dendron **5** (c = 33 µM). In order to record the UV-vis. spectra, the baseline is first established with 2 mL H_2O. The curves that are recorded correspond to the witness, and characteristic bands at 208 nm and 235 nm are observed for the Pd^{II} salt. A solution (D) corresponding to K_2PdCl_4 + dendrimer **1** is prepared in water (c(Pd^{II}) = 33 µM, c(**1**) = 3.6 µM) and also a solution (E) of K_2PdCl_4 + **5** in water (c(Pd^{II}) = 33 µM, c(**5**) = 3.6 µM). The interaction between the dendrimer **1** and the Pd^{II} salt is investigated by preparing first the solution (B) as blank, which allows to record the spectra of the solution (A), (D) and (D) + $NaBH_4$ (c = 330 µM). Secondly, the solution (C) is used as blank, and the spectra of the solutions (A), (E) and (E) + $NaBH_4$ (c= 330 µM) are recorded.

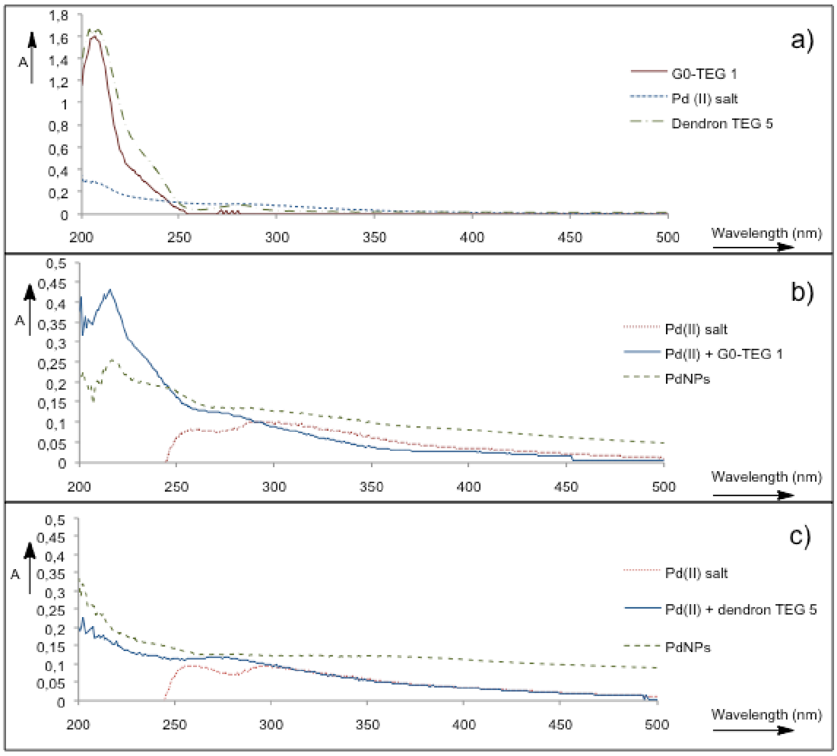


UV-vis. spectrum of **1**, **5**, and K_2PdCl_4

UV-vis. spectrum of the standard materials (G0-TEG ***1*** *= dendrimer with TEG termini, Pd(II) salt =* K_2PdCl_4*, dendron TEG 5 = dendron TEG with bromide termini instead of alkyne or alcohol in order to avoid complexation with Pd). The UV-vis. spectra have been recorded with water as blank. The concentration of G0-TEG* ***1*** *is 3.6 nM, thus the concentration of dendron is 33 nM in order to keep the same quantity of TEG chains. The concentration of* K_2PdCl_4 *is also 33 nM, because in the procedure of PdNPs synthesis we are using 1 Pd per triazole i.e. 9 times more Pd than dendrimer.*



UV-vis. spectrum of K_2PdCl_4 with a concentration that is 10 times higher (330 nM) than that used for the previous UV-vis. spectrum. Two bands are now visible: 208 nm and 235 nm.



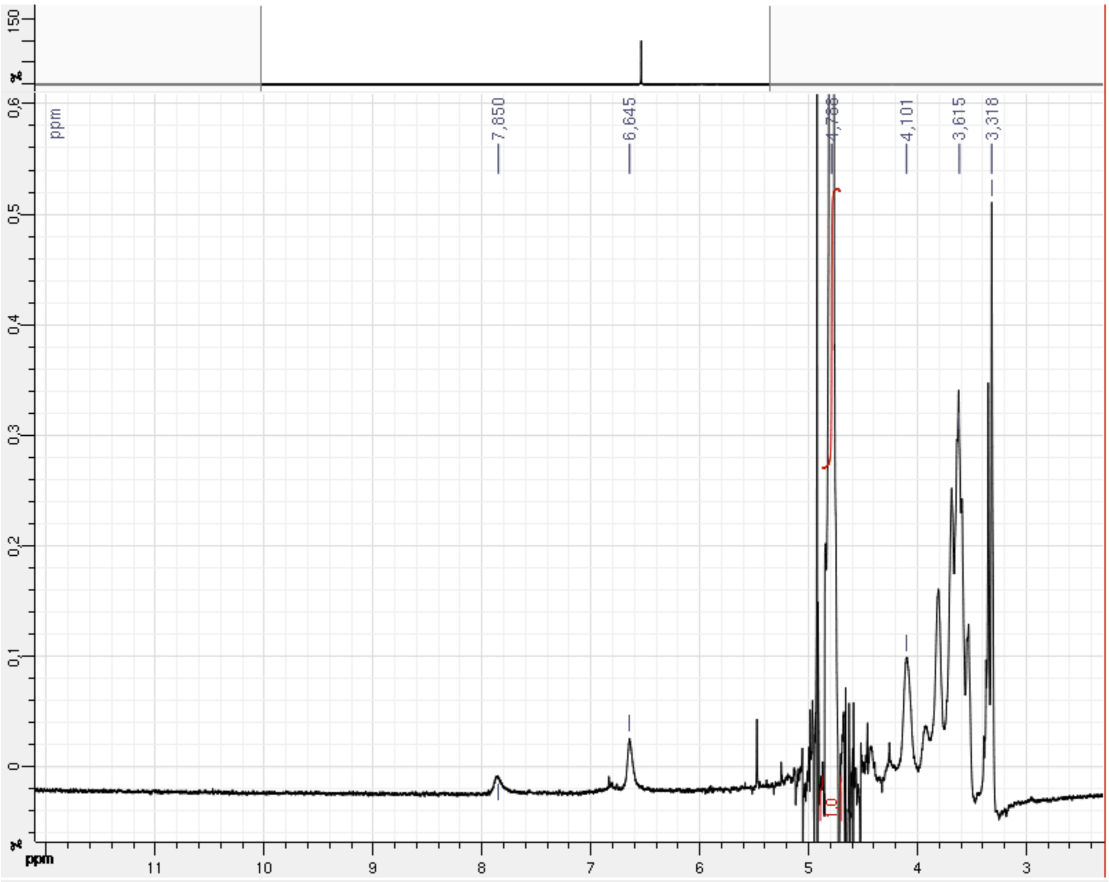
UV-vis. analysis showing the stabilization of Pd^{II} inside the G0-27 TEG **1** by the triazolyl ring.

***a)** UV-vis. spectrum of the starting materials (**1**, $K_2Pd^{II}Cl_4$, and **5**) that are recorded with water as a blank. The concentration of **1** is 3.6 nM, i.e. that of **5** is 33 nM in order to obtain the same quantity of TEG chains. The concentration of $K_2Pd^{II}Cl_4$ also is 33 nM because in the procedure of PdNPs synthesis the stoichiometry is 1 Pd per triazole, i.e. 9 Pd per dendrimer. **b)** UV-vis. spectrum of $K_2Pd^{II}Cl_4$ alone, $K_2Pd^{II}Cl_4$ in the presence of **1**, and K_2PdCl_4 in the presence of **1** after reduction with $NaBH_4$ (PdNPs). The UV-vis. spectra are recorded using **1** as a blank with same concentration as in **a)**. **c)** UV-vis. spectrum of $K_2Pd^{II}Cl_4$ alone, $K_2Pd^{II}Cl_4$ in the presence of **5** and $K_2Pd^{II}Cl_4$ in the presence of **5** after reduction with $NaBH_4$ (PdNPs). The UV-vis. spectra are recorded with **5** as blank with same concentration as in **a)**.*

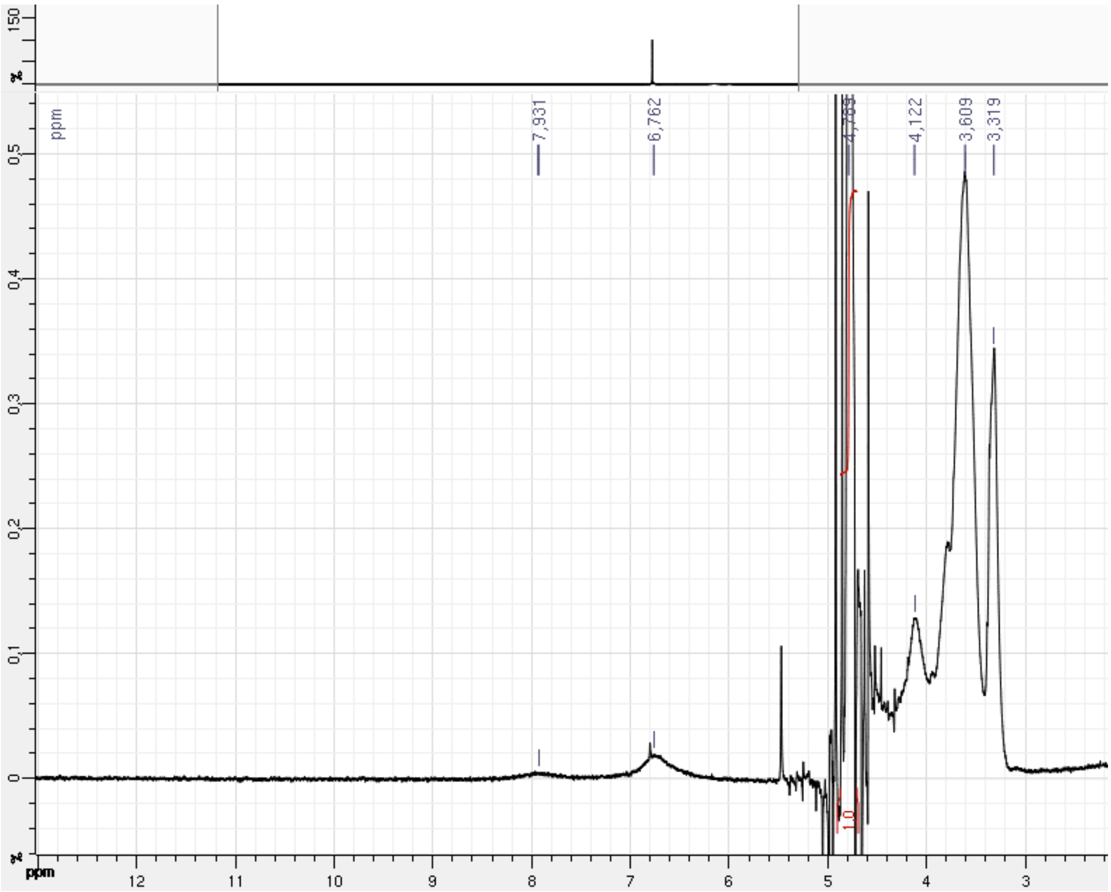
Only one absorbance peak is observed for Pd^{II} at λ_{max} = 206 nm because of its low concentration, whereas at high concentrations, two characteristic bands are present at 208 nm (as here) and at 235 nm. When UV-vis. spectra are recorded with G0-TEG dendrimer **1** as a blank, a new band clearly appears at 217 nm upon mixing the aqueous solution of K_2PdCl_4 with that of **1** (after stirring 5 min, see b)). On the other hand, when Pd^{II} only is in the presence of the TEG dendron **5** (with **5** as blank) no band appears (see S.I.). The band observed at 217 nm when K_2PdCl_4 is added to the dendrimer in water is assigned to a ligand-to-metal charge transfer (LMCT) transition of Pd^{II}. Here, it is associated to the complexation of the metal ions to the interior triazole of **1**. **The UV-vis. spectrum of the mixture of K_2PdCl_4 and TEG dendron 5 c) does not correspond to the UV-vis. spectrum of the mixture of K_2PdCl_4 with 1. In particular, no band is observed at 217 nm in the mixture of K_2PdCl_4 with 5. These experiments show the intradendritic complexation of Pd^{II} at the triazole sites of 1, and they also indicate that there is no strong Pd^{II} complexation of the terminal TEG groups. Moreover, some black PdNPs is observed in the solution of PdNPs stabilized by dendron 5 after 1 day.**

^{1}H NMR spectra showing the stabilization of Pd^{II} at the triazole level.

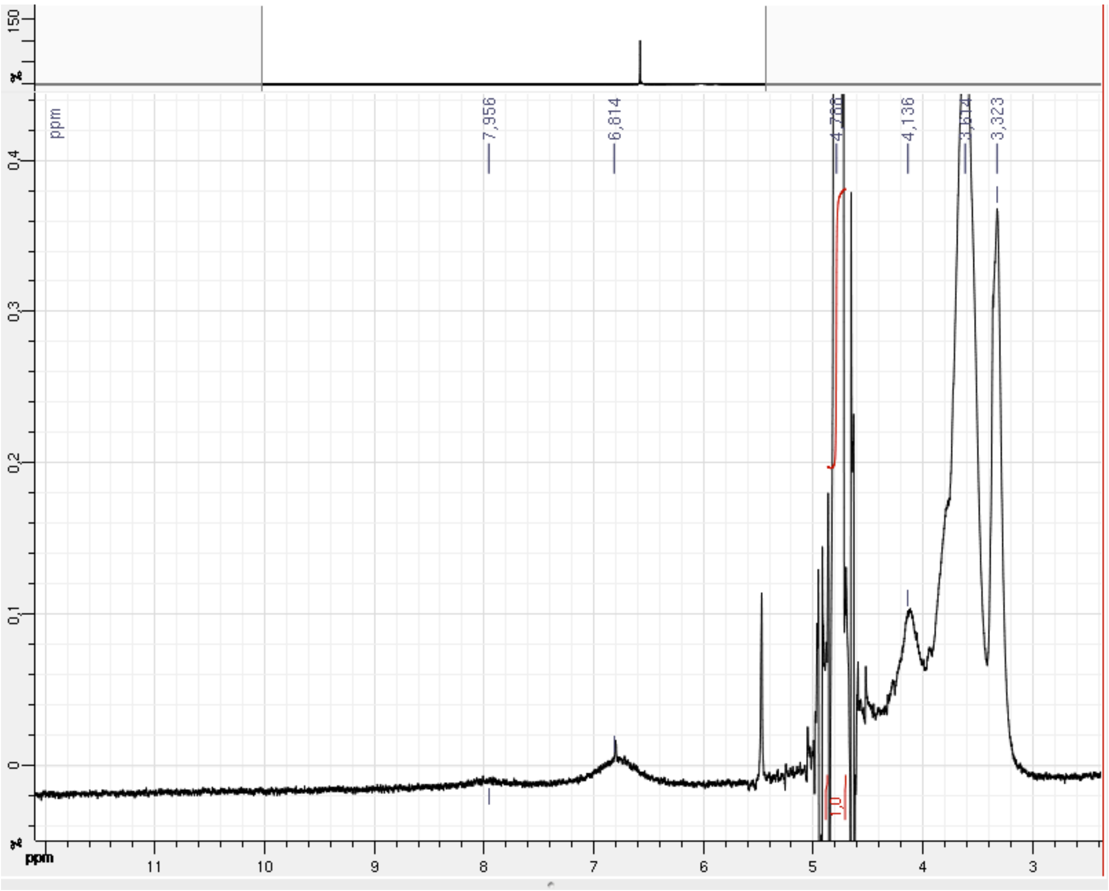
In the ^{1}H NMR spectrum, a shift of the triazolyl proton is observed upon adding 1, 5, and 9 equivalents of K_2PdCl_4 per G0 dendrimer **1** (7.85 ppm, 7.93 ppm, 7.96 ppm), and the peak becomes broader when Pd^{II} is added, which confirms interaction between the triazole group and Pd^{II}. When more than 9 equiv. Pd^{II} are added to **1**, a shift of the ^{1}H NMR signal of the proton of **4** is observed (H from the TEG, and H from the aromatic ring linking the TEG) until 27 equiv. Pd per dendrimer **1** is added.



^{1}H NMR spectrum of **1** in D_2O with zero equivalent of Pd^{II} per dendrimer.



^{1}H NMR spectrum of **1** in D_2O with 5 equivalents of Pd^{II} per dendrimer.



^{1}H NMR spectrum of **1** in D_2O with 9 equivalents of Pd^{II} per dendrimer.

Number of Pd^{II} per G0-TEG	0 eq Pd^{II}	5 eq Pd^{II}	9 eq Pd^{II}
^{1}H NMR: triazole peak	7.850 ppm	7.931 ppm	7.956 ppm
^{1}H NMR external aromatic peak	6.645 ppm	6.762 ppm	6.814 ppm

Table S2: peak shift due to Pd^{II} complexation of the nine triazolyl group of the G0-27 TEG **1**

Pd^{II} forms a complex with the triazolyl group inside the dendrimer G0-TEG **1**. The external aromatic ring is not located far from the triazolyl group, which explains why a shift is observed upon adding more Pd^{II} (table 2).

7. Other TEM pictures of PdNPs

Attempts to increase the number of Pd by dendrimer

Attempts to increase the number of PdNPs by increasing the Pd^{II} loading, for instance with a 3-fold excess of Pd^{II} vs. triazole groups led to quite stable PdNPs that are larger (TEM: 3.5 ± 1 nm, see Figure 8) than upon stoichiometric addition, clearly confirming that the number of Pd atoms is not related to the number of triazole groups. These PdNPs are moreover less stable than those synthesized with a stoichiometry 1/1 = triazole/Pd. Attempts to increase even more the Pd loading by using a 5-fold excess of Pd vs. the number of triazole groups led to the formation of very large PdNPs (TEM: 15-17 nm, see Figure 9) that started to aggregate after one week. To conclude, if PdNPs are synthesized for future catalytic experiments, PdPNs must be synthesized with a stoichiometry 1/1 = triazole/Pd.

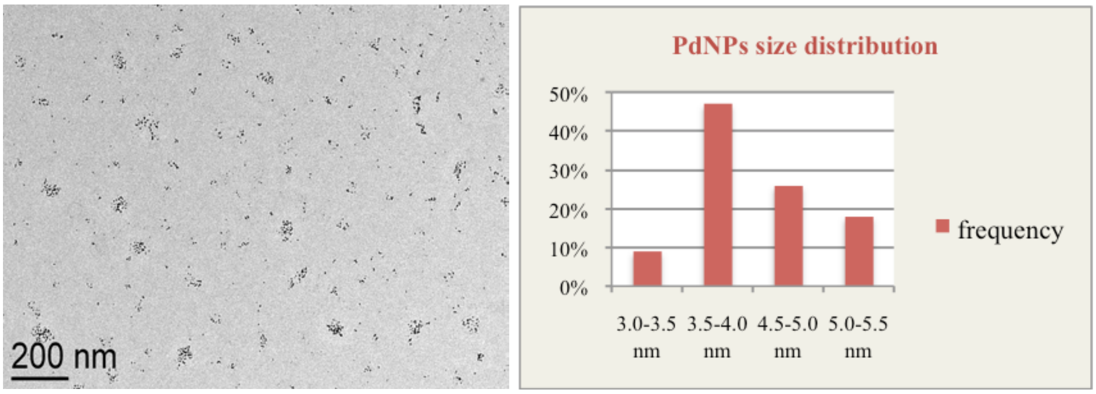


Figure S8: TEM analysis of PdNPs with 3 eq of Pd^{II} per triazole stabilized by G0-27 TEG 1 (left) and their size dispersity on 320 PdNPs (right), average value: 3.5 ± 1 nm.

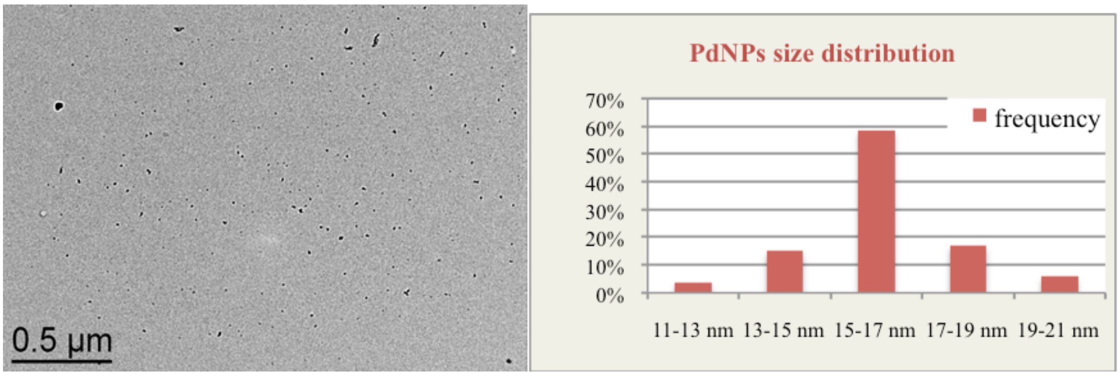


Figure S9: TEM analysis of PdNPs with 5 eq of Pd^{II} per triazole stabilized by G0-27 TEG 1 (left) and their size dispersity on 176 PdNPs (right), average value: 16 ± 1 nm.

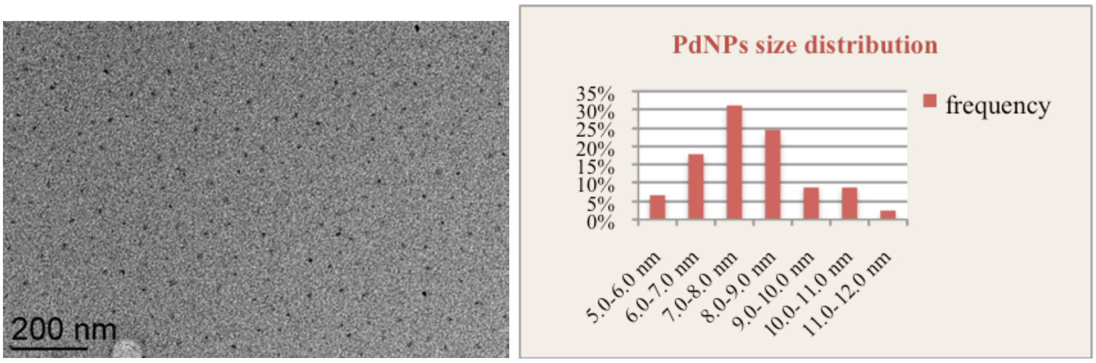
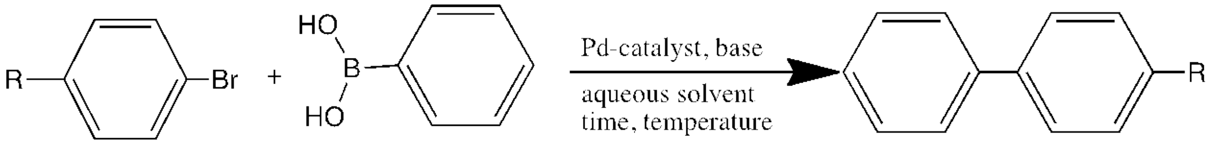


Figure S10: TEM analysis of PdNPs used 5 times (left) and their size dispersity on 182 PdNPs (right), average value: 8 ± 1 nm.

TEM analyses show that the PdNPs arelarger after the reaction (8 ± 1 nm) than before (1.4 nm ± 0.7 nm) but their sizes examined by TEM no longer increase after further catalytic runs (figure S11). These PdNPs recycled still active at 5 ppm level for bromoarenes and decreased with 1 ppm.

8. Comparative table with literature



R[ref]	catalyst	Temp. (°C)	TON	TOF (h^{-1})
4-H[S2]	PSSA-co-MA-Pd^0	100	99	5940
4-OMe[S3]	Pd-SDS	100	38	456
4-OMe[6i]	Pd-PVP (MTPs)	100	1680	1680
4-Me[S4]	Pd-PEG	25	90	45
4-NO$_2$[S5]	Pd-1/FSG	100	990	123
4-OMe[S6]	Fe$_3$O$_4$-Pd	50	144	12
4-OMe[S7]	pEVPBr-Pd	90	340	38
4-OMe[S8]	Pd-PS	100	50	10
4-COMe[S9]	HAP-Pd0	100	139	23
4-OMe[4k]	PdCl$_2$(py)$_2$@SHS	60	4681	14050
4-COMe[6g]	Pd/IL	120	970	970
4-OMe[6h]	Pd-MEPI	100	24250	8083
4-COMe[6a]	Pd-salt	90	4250	1062
4-OMe[S10]	Pd@PNIPAM	90	300	30
4-Me[S11]	Pdx - ([PW$_{11}$O$_{39}$]$^{7-}$)$_y$	80	89	7
4-OMe[S12]	Pd-block-co-poly	90	310	31
4-COMe[6f]	Pd-G3-p3	80	85000	2125
4-OMe[6f]	Pd-G3-p3	80	82	10
4-H[4i]	Pd@CNPCs	50	982	327
4-Me[S13]	PS-PdONPs	80	59	59
4-Me[4j]	Pd-TiO$_2$	80	115	29
4-OMe[S14]	Pd@PMO-IL	75	475	95
4-NH$_2$[S15]	Pd-XH-15-SBA	90	96	7
4-OMe[S16]	Pd^{2+}-G0	80	386	99
4-Me[S17]	Pd(0)/Al$_2$O$_3$ –ZrO$_2$	60	45	12
4-OMe[6g]	Pd(OAc)$_2$/L	100	19600	2800
4-OMe[6b]	Pd(OAc)$_2$/CNC-pincer	100	1000	500
4-H[6b]	Pd(OAc)$_2$/CNC-pincer	100	1 x10^9	1.7 x 10^8
4-NO$_2$[6e]	Pd(OAc)$_2$/CNC-pincer	100	1000	500

Table S3: Some examples of Suzuki-Miyaura coupling of bromoarenes. The reactions have been conducted with various catalysts at different temperatures in aqueous solvents.

9.Comparative table with our previous works

We have previously stabilized PdNPs by dendrimers with various triazolyl termini. Firstly PdNP was stabilized by dendrimers containing triazolyl ferrocenes[6c] (G0-9 Fc, G1-27 Fe) and bifferocenes[S18] (G0-9 biFc, G1-27 biFc). These dendrimers are not soluble in water, thus only PdNPs synthesize in a mixture of solvent $CHCl_3$/MeOH is considered. The solution of PdNPs must be kept under N_2 and fresh PdNPs are used for catalysis. Concerning PdNPs stabilized by dendrimers containing triazolyl sulfonated termini,[6d] the PdNPs synthesis is the same as that used for the synthesis of PdNPs stabilized by G0-27 TEG and G1-81 TEG, thus the comparison is more suitable.

dendrimer	PdNP size	Solvent Used for the synthesis	storage	Air stable	Iodoarene[a] TON **TOF**	Bromoarene[b] TON **TOF**
[6c]G0-9 Fc	2.8 nm	$CHCl_3$/MeOH	No	No	540 000 **1042 h^{-1}**	265 **15 h^{-1}**
*[6c]G1-27 Fc	1.3 nm	$CHCl_3$/MeOH	No	No	5200 **363 h^{-1}**	-
[S18]G0-9 biFc	-	-	-	-	-	-
[S18]G1-27 biFc	In situ	$CHCl_3$/MeOH	No	No	5300 **221 h^{-1}**	-
[6d]G0-9 SO_3^-	2.3 nm	H_2O	No	No	9200 **1533 h^{-1}**	10 000 **8 700 h^{-1}**
[6d]G1-27 SO_3^-	2.8 nm	H_2O	No	No	9400 **1567 h^{-1}**	-
G0-27 TEG **1**	1.4 nm	H_2O	yes	yes	2 700 000 **28 000 h^{-1}**	990 000 **16 000 h^{-1}**
G1-81 TEG **2**	2.7 nm	H_2O	yes	yes	2 700 000 **28 000 h^{-1}**	200 000 **3 333 h^{-1}**

Table S4: Comparison between different stabilization of PdNPs.
[a]The Suzuki-Miyaura reaction was carried out between iodobenzene and acid phenyl boronic.
[b]The Suzuki-Miyaura reaction was carried out between bromobenzene and acid phenyl boronic.
*The dendrimer G1-27 Fc is composed of external triazolyl function as in the other dendrimers, but also internal triazolyl, which leads to a different stabilization.

The results obtained with PdNPs stabilized by hydrophobic dendrimers, the Suzuki-Miyaura coupling is not as good, and the reaction is carried out in a mixture solvent of $CHCl_3$/MeOH. Moreover PdNPs are less stable than in this present case. PdNPs stabilized by G1-27 Fc have size similar to that of PdNPs stabilized by G0-27 TEG, but the activity is completely different; no activity is observed with bromobenzene. As explained above, the comparison is of interest with G0-9 SO_3^- and G1-27 SO_3^-. The size of PdNP is larger than the actual size, which is an indication of the important role of the TEG termini of the dendrimers **1** and **2**. The activity in the Suzuki-Miyaura reaction is also very low with the PdNPs stabilized by the sulfonated dendrimers. The stability of the PdNPs stabilized by 1 and 2 are far better from what was obtained earlier, leading to a possible storage without strain for months.

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