Experimental details. Growth modulus in supercritical fluid (Figure 1, 1 in the paper) is composed of one pump for palladium trifluoroacetate solubilized in acetone injection. All the experimental process is made with 316 Stainless steel high pressure pipe (interior diameter equal to 0.32 cm). The tubular reactor where thermal decomposition occurs is maintained at constant pressure (20 MPa) with a pressure regulator and at constant temperature with a hot-air oven (250°C). After the pressure regulator, the fluid is sprayed (Figure S1) into a closed vessel where the functionalizing solution is stirred with an agitator (Figure 1, 2 in the paper). Palladium trifluoroacetate and heptadecafluoro-1-decanethiol are purchased from Merck and Fluka and used without further purification.

Figure S1. Design and operating conditions of the spray nozzle.
**XRD measurements.** Powder XRD patterns (Figure S1) are obtained using a PANalytical X’Pert Pro MPD diffractometer with a 0/20 Bragg-Brentano geometry, a copper target tube, and an incident beam monochromator (λ (Kα1) = 1.54059 Å), (step: 0.0017°).

![X-Ray diffraction pattern of the nanoparticles corresponding to metallic Pd.](image)

**XPS measurements.** The measurements (Figure S2) are performed on sample powder inlayed into an indium foil with an ESCALAB 220i-XL apparatus. The electron analyser was operating at a constant pass energy of 20 eV. The sample is exposed to monochromatized Al Kα X-ray excitation (1486.6 eV with a size spot of 250 μm). The binding energies are referenced to the C1s signal due to ambient hydrocarbons (C-H and C-C) at 284.6 eV.

![X-ray photoelectron spectra of the nanoparticles showing the Pd3d 3d5/2 (335.2 eV) and 3d3/2 (340.5 eV), typical values for metallic Pd.](image)
**Microscopy measurements.** TEM images were performed with a TECNAI F20 (FEG) operating at 200 kV. A drop of the colloidal solution (nanoparticles in acetone) was deposited on a copper grid covered by an ultra thin carbon film over a holey carbon film. Size distribution is determined by manual counting on 150 particles.

![Size distribution of non-functionalized palladium nanoparticles organized as aggregates.](image1)

Figure S4. Size distribution of non-functionalized palladium nanoparticles organized as aggregates.

![TEM image and particle size distribution of palladium nanoparticles stabilized in BMIMPF$_6$.](image2)

Figure S5. TEM image and particle size distribution of palladium nanoparticles stabilized in BMIMPF$_6$.

**DLS measurements.** Dynamic Light Scattering experiments were carried out on a Zetasizer 3000 HSA. The light source is a 10 mW HeNe laser operating at 633 nm with a scattering angle $\theta = 90^\circ$. The mean size and error are determined with the accumulation of 10 scans during 12 hours. To check the stability in time of samples, measurements are performed each week for six months. The data used for DLS exploitation are reported in Table S1.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Refractive index</th>
<th>Viscosity@25°C $^{[a]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>1.36</td>
<td>0.316</td>
</tr>
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</table>

$^{[a]}$ measured by an Advanced Rheometer AR1000 TA instrument.
The size distribution and the autocorrelation functions of thiol-capped and nonfunctionalized palladium NPs are presented in Figures S5 a and b.

![Figure S6. DLS measurements: a) Size distributions obtained for thiol-capped NPs (grey) and naked NPs (black); b) autocorrelation function for thiol-capped NPs and naked NPs.](image)

**Catalysis.** Catalytic activity was tested with functional palladium nanoparticles (1% in mass of reactive agents) using Heck reaction between iodobenzene (3 mmol) and styrene (3 mmol) using triethylamine as a base. The reaction products are isolated by simple extraction of BMIMPF₆ with diethyl ether. The product was analysed by \(^1\)H NMR and gas chromatography. GC analysis was performed with a Varian Chrompack (CP-3800) apparatus equipped with a SGE nonpolar capillary column (BPX5 30 mA 0.25 mm) with the following conditions of analysis: injector temperature of 250°C; splitless injection mode; helium as carrier gas at 1 mL/min; initial oven temperature of 80°C, 6 min; rate 1: 20°C/min; final temperature 1: 150°C, 10 min; detector temperature: 300°C). Turn over number (TON, defined as the mole of iodobenzene consumed by moles of surface palladium and by hour), was calculated.

**NMR measurement.** \(^1\)H NMR spectra were recorded on a Bruker ARX 500 equipped with a cryosonde (512 scans, delay between two pulses D1 = 2s, T = 298.3 K). Analysis of the spectra were done with MestReC 4.5.9.5.