Electronic Supplementary Material (ESI) for Nanoscale.

The Five shades of oleylamine in a morphological transition of cobalt nanospheres to nanorods.

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METHODS

Synthesis. *Synthesis cobalt precursors*. [$CoCl_2.6H_2O$] (Sigma-Aldrich, 98%), PPh_3 (fluorochem, 95%), $NaBH_4$ (Acros Organic, 95%) were commercially bought. Ethanol absolute and diethylether were degassed. OAm (70-98%) from Sigma-Aldrich was degassed under Argon

Preparation of [$CoCl(PPh_3)_3$]: On 9.6 g of [$CoCl_2.6H_2O$], (40 mmoles) and 32.0 g of triphenylphosphine (122 mmoles) were added 600 ml of degassed ethanol. The resulting heterogeneous solution was stirred vigorously at 60-70°C for 30 minutes environ to form *in-situ* the complex $CoCl_2(PPh_3)_2$ (II) as a bright blue powder. The mixture was then cooled down to 30°C, and 1.28 g of sodium borohydride was added (34 mmoles) in 10 portions at a 10-minute interval. The color of the mixture changed from bright blue to dark brown. After 2 hours the brown precipitate was filtrated, washed sequentially with ethanol and diethyl ether and was finally dried under vacuum to give 25 g of the desired [$CoCl(PPh_3)_3$] complex with 75% yield. The same procedure was used for the preparation of [$CoBr(PPh_3)_3$] and [$CoI(PPh_3)_3$] with [$CoBr_2.xH_2O$] and [$CoI_2.xH_2O$] (Sigma-Aldrich).

Synthesis of cobalt hcp-NRs. In a glove box under a nitrogen atmosphere, 10 mL of degassed OAm was mixed with [$CoX(PPh_3)_3$] (X = Cl, Br, I) in a 25 mL vial caped with a septum pierced by a pipette (to provide overpressure). The solution was stirred and heated using a 50 mL "drysyn" filled with sand. The mixture was heated by controlling the increase of the temperature from 20 to 190°C in 1h then heat 10h to obtain the NRs. Then, the solution was cooled down to room temperature, and the NPs were washed by adding 20 mL of ethanol and then centrifuged for 5 min at 2500 rpm. The colorless supernatant was removed, and the resulting black solid was then dispersed in toluene. For synthesis, in OAm/tetradecane, a mixture of 1 mL of OA and 9 mL of tetradecane was used instead of pure OAm. The supernatant observed at 10h is blue.

Sample Characterization. *Transmission Electron Microscopy (TEM)*. A 100 kV (TEM, JEOL JEM-1011 with a digital camera Gatan) was used to characterize cobalt nanocrystals and their assemblies (low magnification bright field picture, Selected Area Electron Diffraction, SAED). To observe the nanoparticles, 10 µL of the solution containing dispersed nanoparticles in toluene were deposited on a TEM grid, followed by evaporation of solvent in order to form a nanoparticle film.

Environnemental – Transmission Electron Microscopy (E-TEM). For all the E-TEM observations, a JEOL 3010 operated at 300kV was used. A mixture of solvent (2/3 OAm, 1/3 toluene) with the cobalt precursor *[$CoCl(PPh_3)_3$]* was prepared. Micro drops of solution were encapsulated between two graphene oxide layers, deposited on carbon film.

Small Angle X-Ray Scattering (SAXS). A SAXS system was used from the brand XENOCS (XEUSS line). The device was composed of a generator of 30W with a anode Cu (λ= 0.154 nm), a single multilayer mirror system (<0.4 mrad) and a set of anti-scattering single crystal slots, with motorized movement for adjusting the size of the beam (0.2 x 0.2 mm^2 to 0.8 x 0.8 mm^2). The detector was a Pilatus 300k (83.8 x 106.5 mm^2). The samples were prepared in a glove box under a nitrogen atmosphere. 150 µL of solution was inserted in a mark-tube made of glass (80 mm x 2.00 mm, wall thickness = 0.01 mm) then sealed with a glue gun.

Nuclear Magnetic Resonance (NMR). A 400MHz Bruker Nanobay was used for the analysis. Console Avance III nanobay. A BBFO (H^1 direct probe) probe was used.

Results and Discussion

TEM Characterization

TEM monitoring of Co NPs extracted in pure Oleylamine (OAm); (Data)

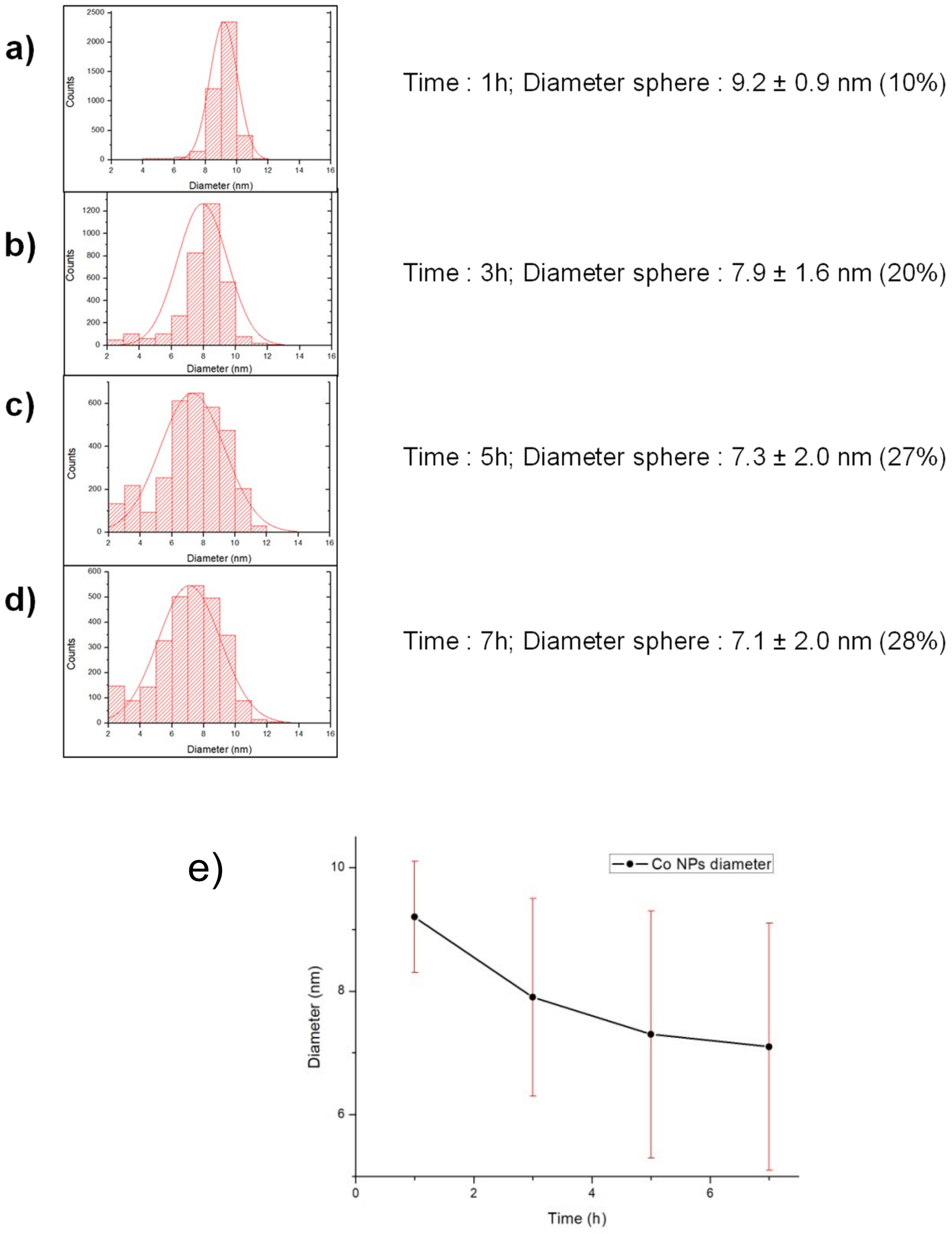
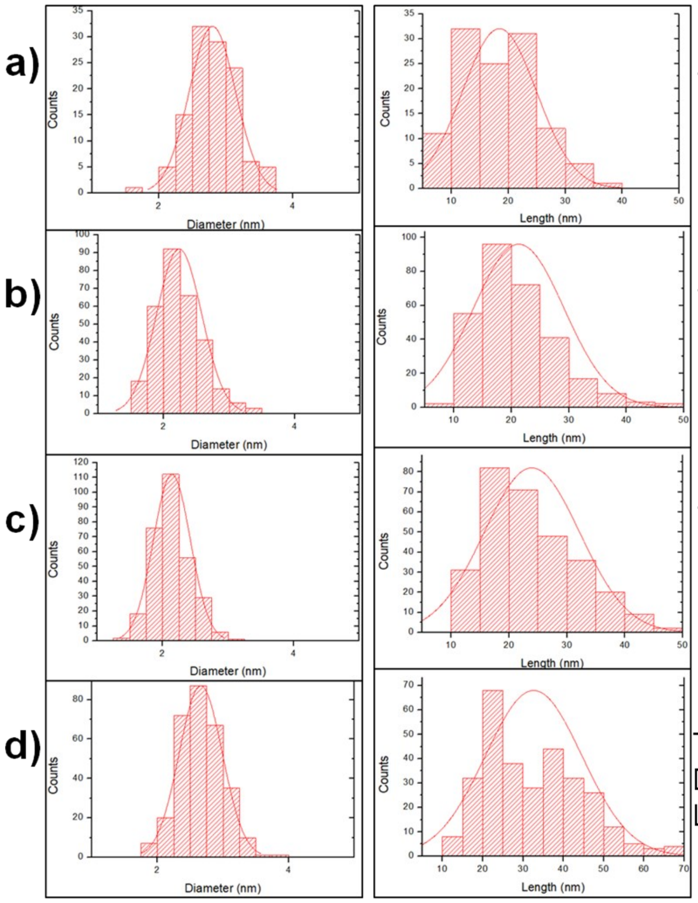


Fig. S1. Data of TEM pictures of spherical Co NPs extracted. The synthesis was performed in 10 mL of OAm with [CoCl(PPh$_3$)$_3$]. At 1h (a), 3h (b), 5h (c) and 7h (d). Size decreasing and polydispersity increasing of Co NPs diameter over time (e).



Time : 3h;
Diameter rods : 2.8 ± 0.3 nm (11%)
Length rods : 18.4 ± 6.5 nm (35%)

Time : 5h;
Diameter rods : 2.2 ± 0.3 nm (14%)
Length rods : 21.3 ± 6.5 nm (35%)

Time : 7h;
Diameter rods : 2.1 ± 0.3 nm (14%)
Length rods : 24.0 ± 8.5 nm (35%)

Time : 10h;
Diameter rods : 2.7 ± 0.3 nm (11%)
Length rods : 32.6 ± 12.0 nm (37%)

Fig. S2. Data of TEM pictures of Co NRs extracted. The synthesis was performed in 10 mL of OAm with [$CoCl(PPh_3)_3$]. At 3h (a), 5h (b), 7h (c) and 10h (d).

TEM monitoring of Co NPs in raw media (pure OAm); (Data)

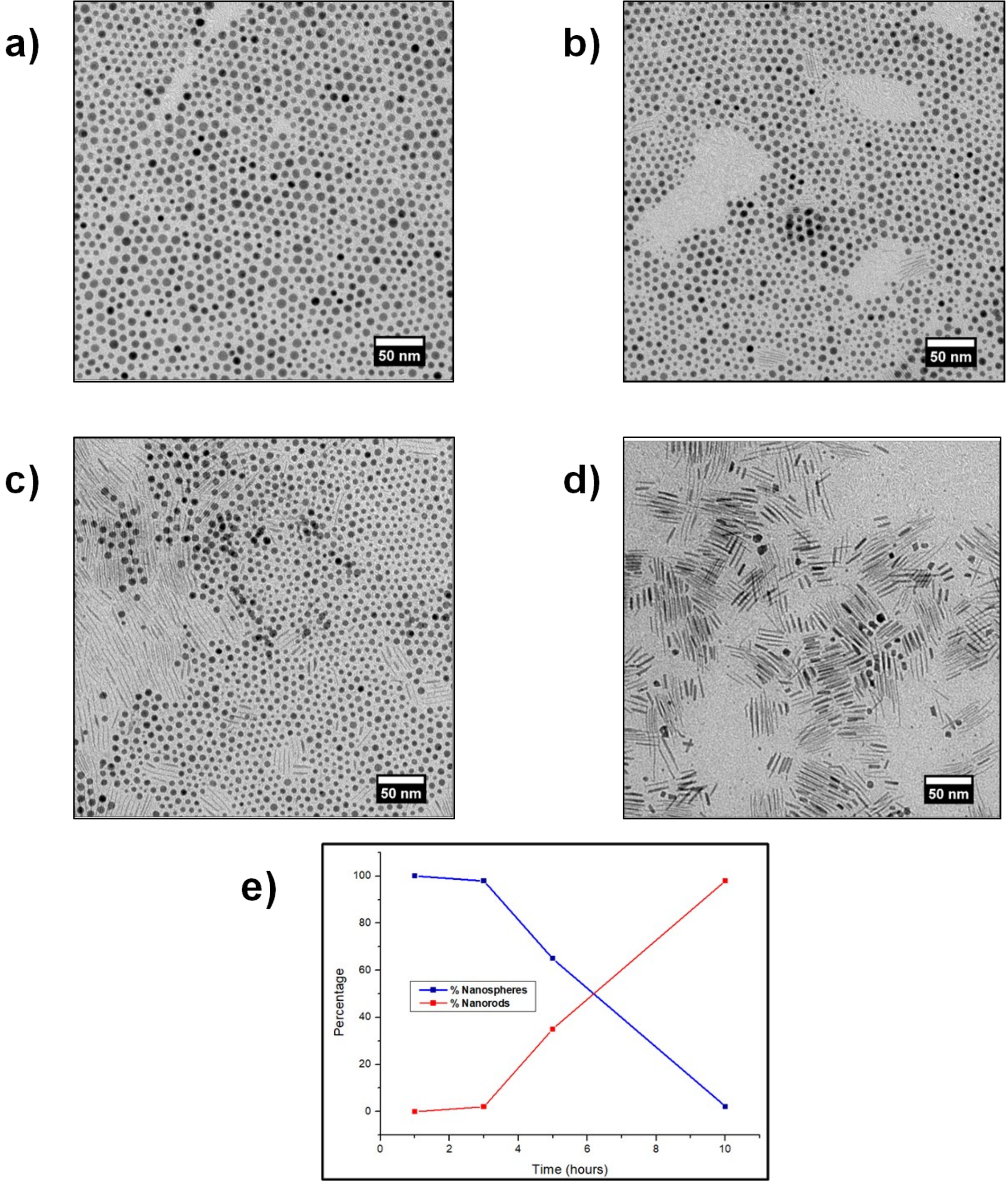
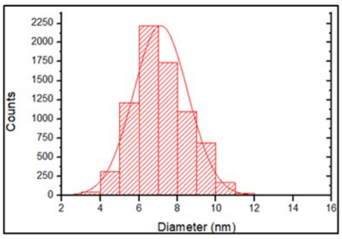


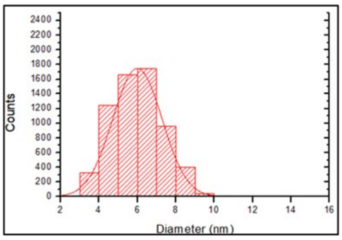
Fig. S3. Co NPs synthesis with 10 ml of OAm and [$CoCl(PPh_3)_3$]. Samples are collected with one drop of solutions and washed with two drops of EtOH at 1h (a), 3h (b), 5h (c) and 10h (d). Ratio sphere/rods overtime; 10h (e).

a)



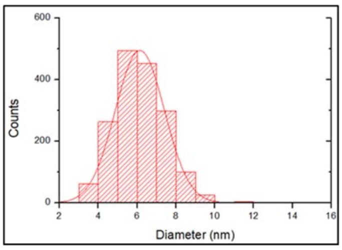
Time : 1h; Diameter sphere : 7.1 ± 1.4 nm (20%)

b)



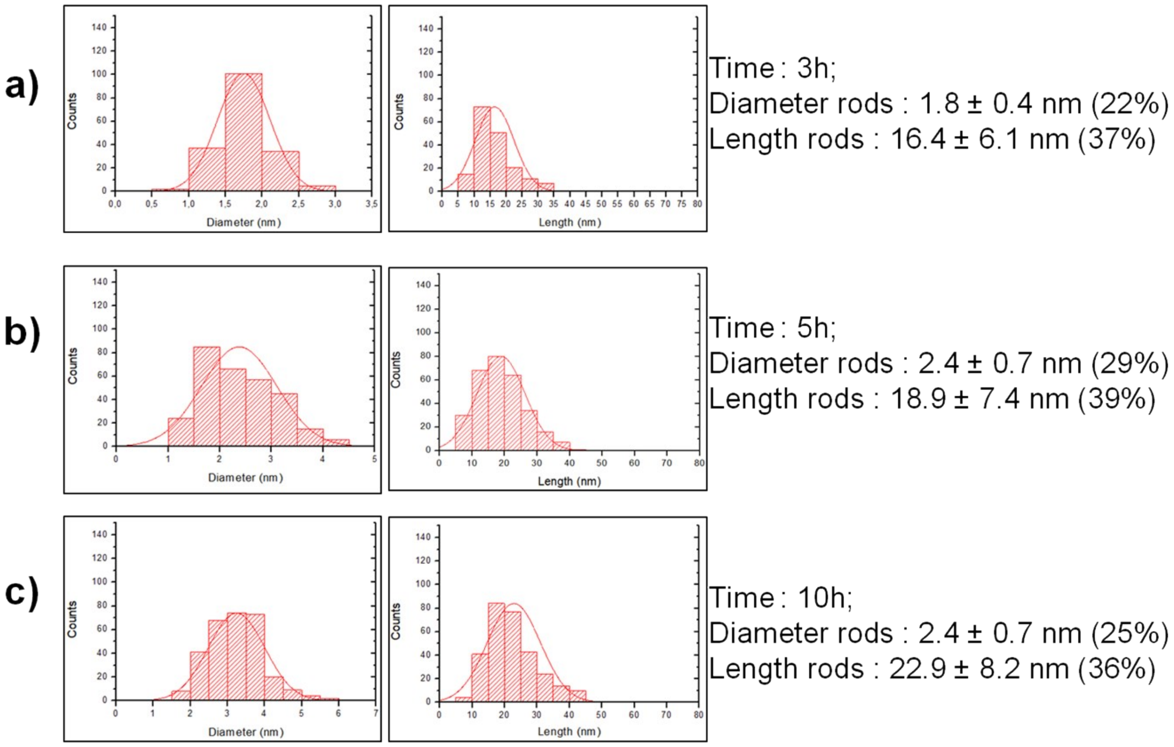
Time : 3h; Diameter sphere : 6.0 ± 1.3 nm (22%)

c)



Time : 5h; Diameter sphere : 6.1 ± 1.3 nm (21%)

Fig. S4. Data of TEM pictures of spherical Co NPs in a raw media. The synthesis was performed in 10 mL of OAm with [CoCl(PPh_3)$_3$]. At 1h (a), 3h (b) and 5h (c).



Time : 3h;
Diameter rods : 1.8 ± 0.4 nm (22%)
Length rods : 16.4 ± 6.1 nm (37%)

Time : 5h;
Diameter rods : 2.4 ± 0.7 nm (29%)
Length rods : 18.9 ± 7.4 nm (39%)

Time : 10h;
Diameter rods : 2.4 ± 0.7 nm (25%)
Length rods : 22.9 ± 8.2 nm (36%)

Fig. S5. Data of TEM pictures of Co NRs in a raw media. The synthesis was performed in 10 mL of OAm with [CoCl(PPh$_3$)$_3$]. At 3h (a), 5h (b) and 10h (c).

TEM images N,N-dimethylhexadecylamine synthesis

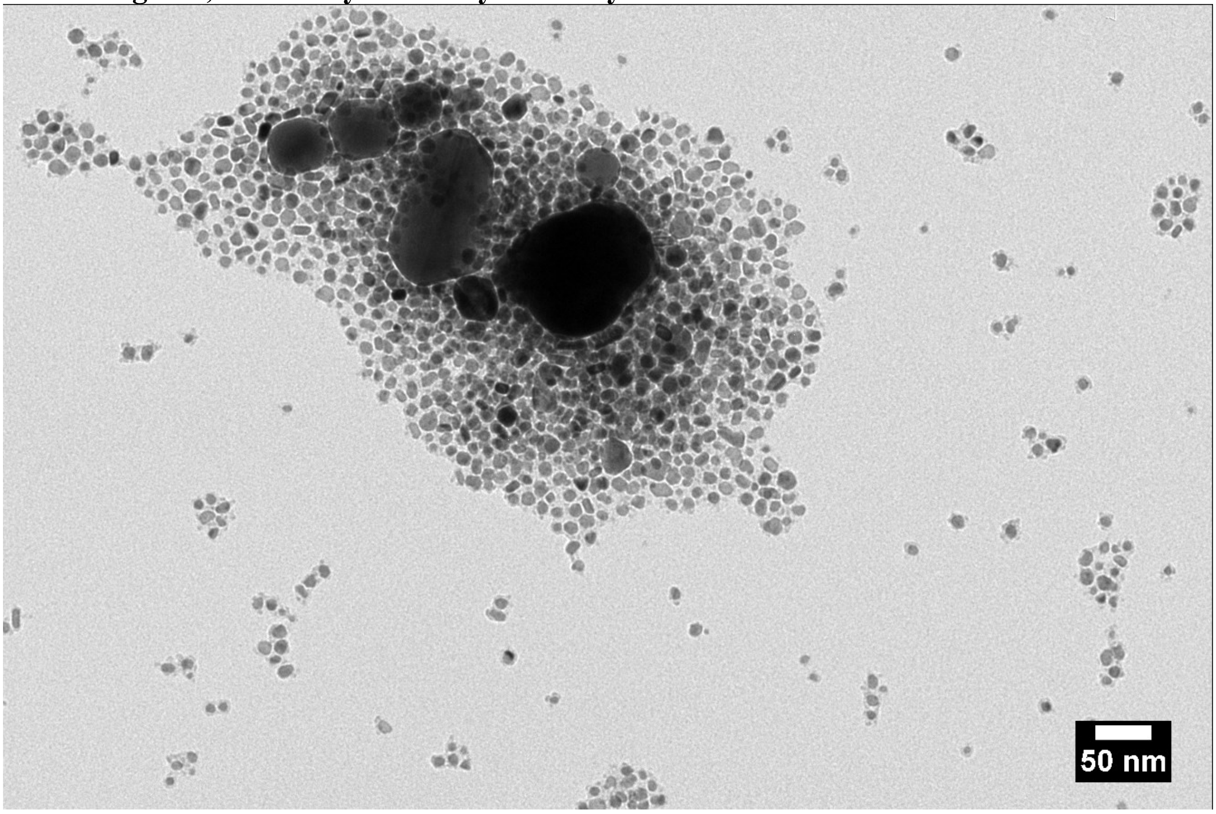
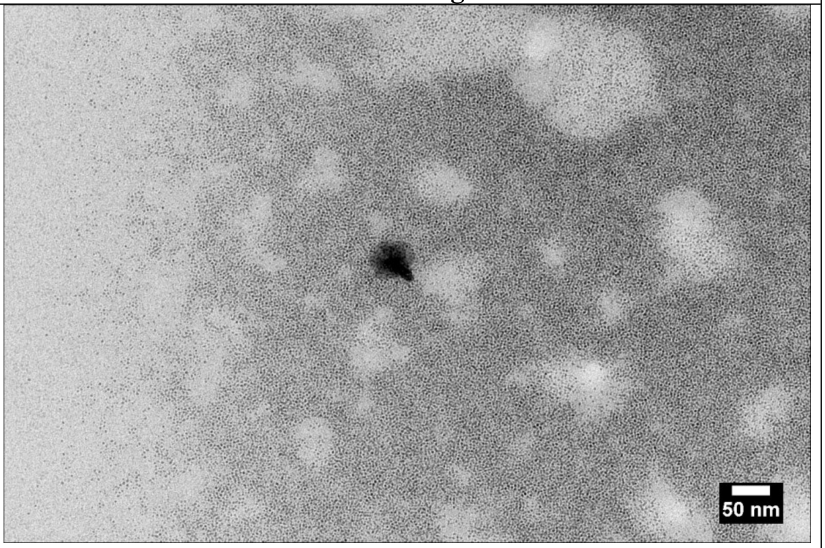
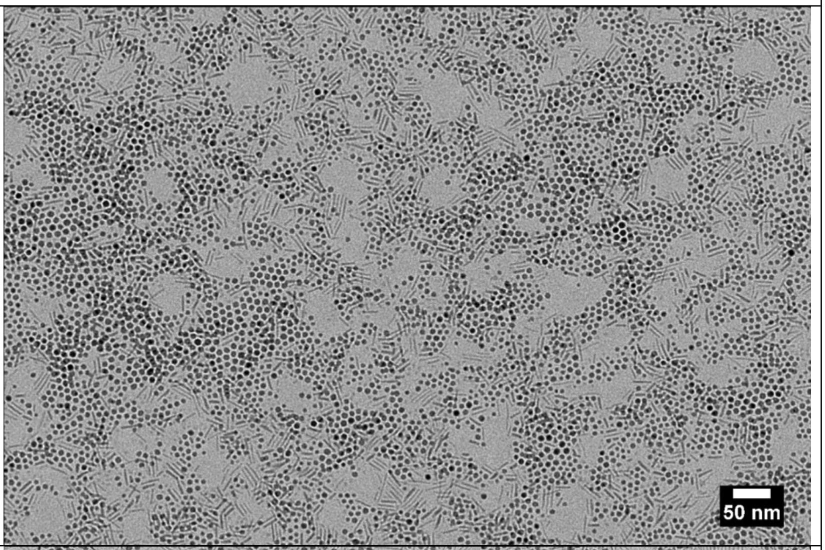
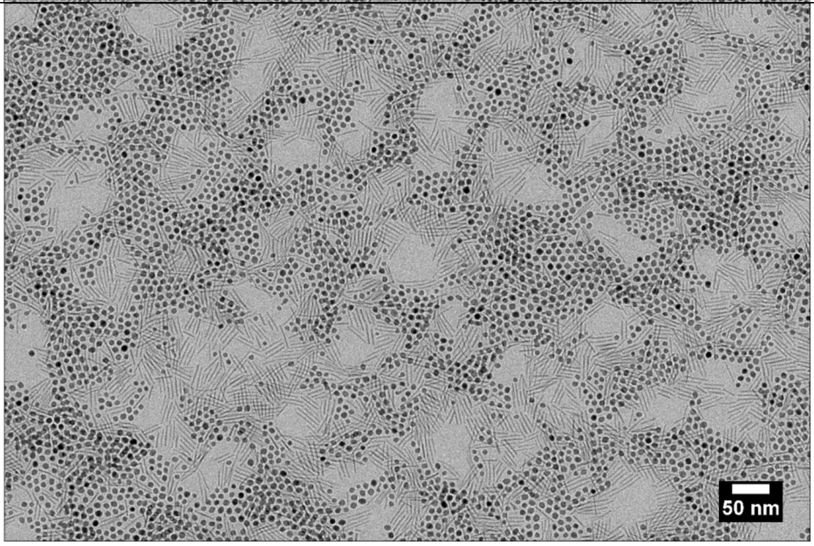


Fig. S6. TEM images of NPs synthesis with N,N-dimethylhexadecylamine and $[CoCl(PPh_3)_3]$ for 10h at 190°C.

TEM images of different long chain amines

Entry	Solvent	TEM image
1	Octylamine (C8)	
2	Dodecylamine (C12)	
3	Tetradecylamine (C14)	

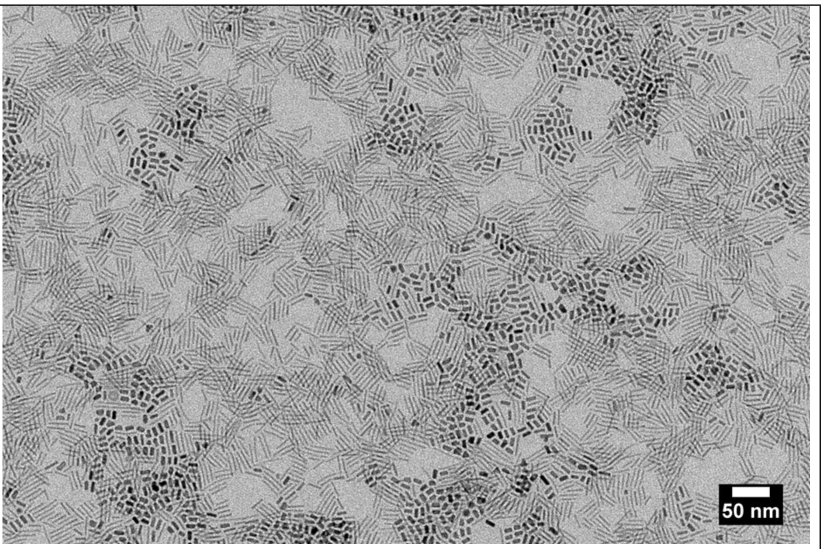
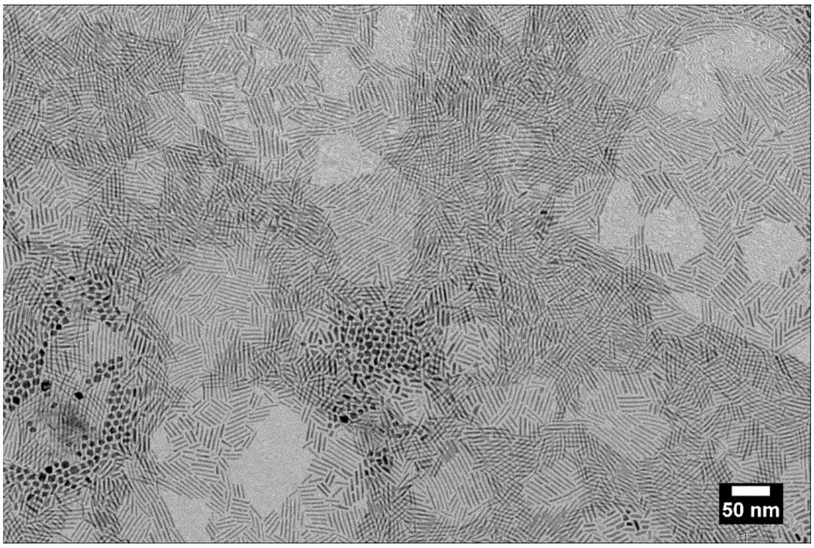
4	Hexadecylamine (C16)	
5	Octadecylamine (C18)	

Table S1. TEM images of NPs synthesis with different long chain amines and [CoCl(PPh_3)$_3$]. All synthesis was performed for 10h at 190°C, except for C8 (140°C) because boiling point is at (176°C).

TEM monitoring of Co NPs extracted. Synthesis ratio 9:1.

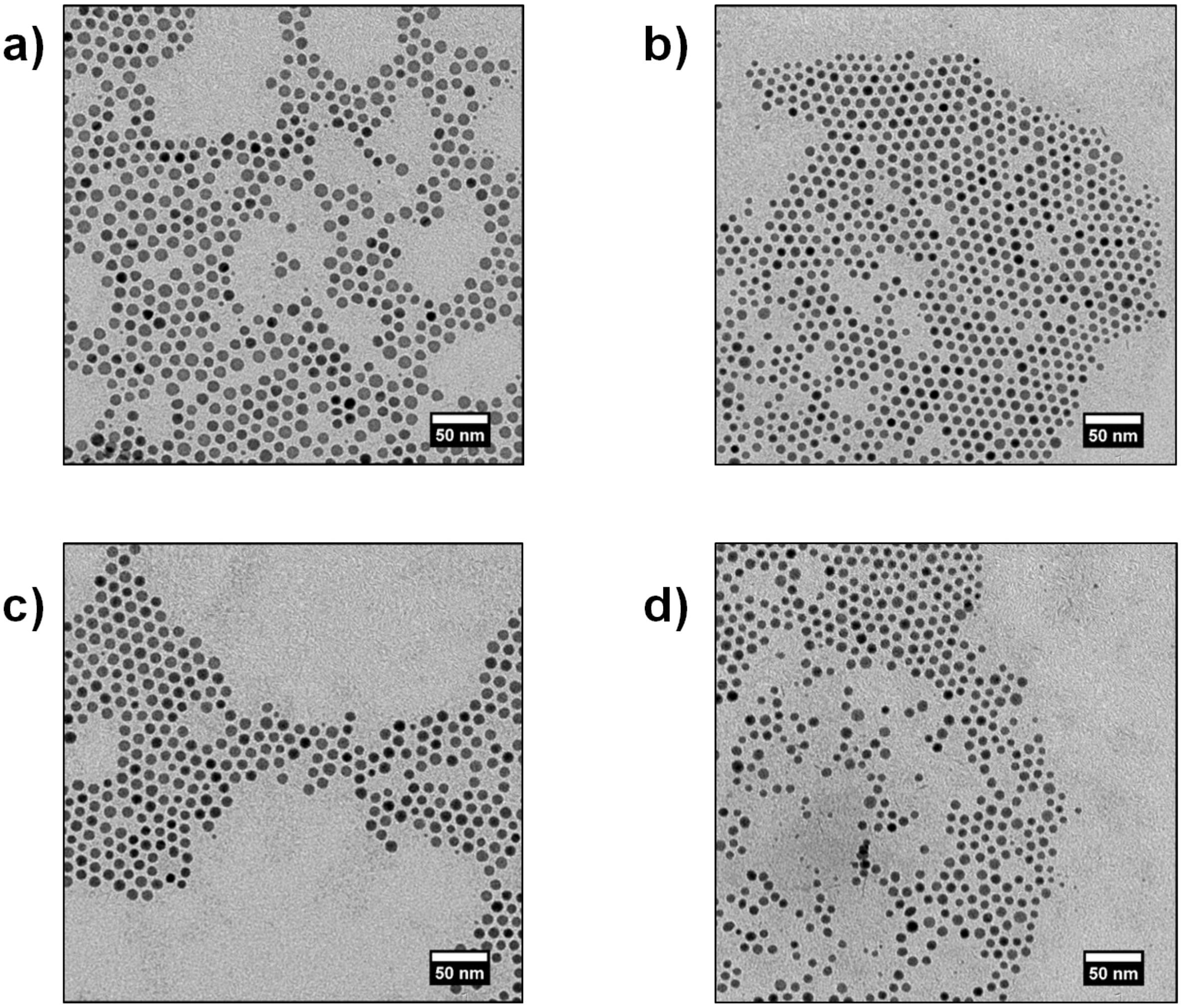
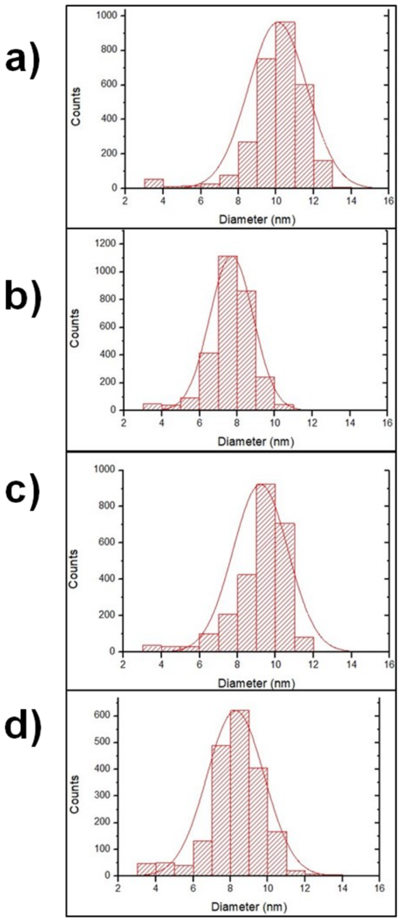


Fig. S7. Co NPs synthesis in 9 mL of tetradecane and 1 ml of OAm (ratio 9:1) and [$CoCl(PPh_3)_3$]. Samples were collected and washed with EtOH at 1h (a), 3h (b), 5h (c) and 10h (d).



Time : 1h; Diameter sphere : 10.1 ± 1.6 nm (15%)

Time : 3h; Diameter sphere : 7.7 ± 1.2 nm (16%)

Time : 5h; Diameter sphere : 9.2 ± 1.4 nm (15%)

Time : 10h; Diameter sphere : 8.3 ± 1.5 nm (15%)

Fig. S8. Data of TEM images of Co NPs extracted. The synthesis was performed in 9 mL of tetradecane and 1 mL of OAm (ratio 9:1) with [CoCl(PPh_3)$_3$].

TEM images of Co NPs extracted. Synthesis ratio 7:3

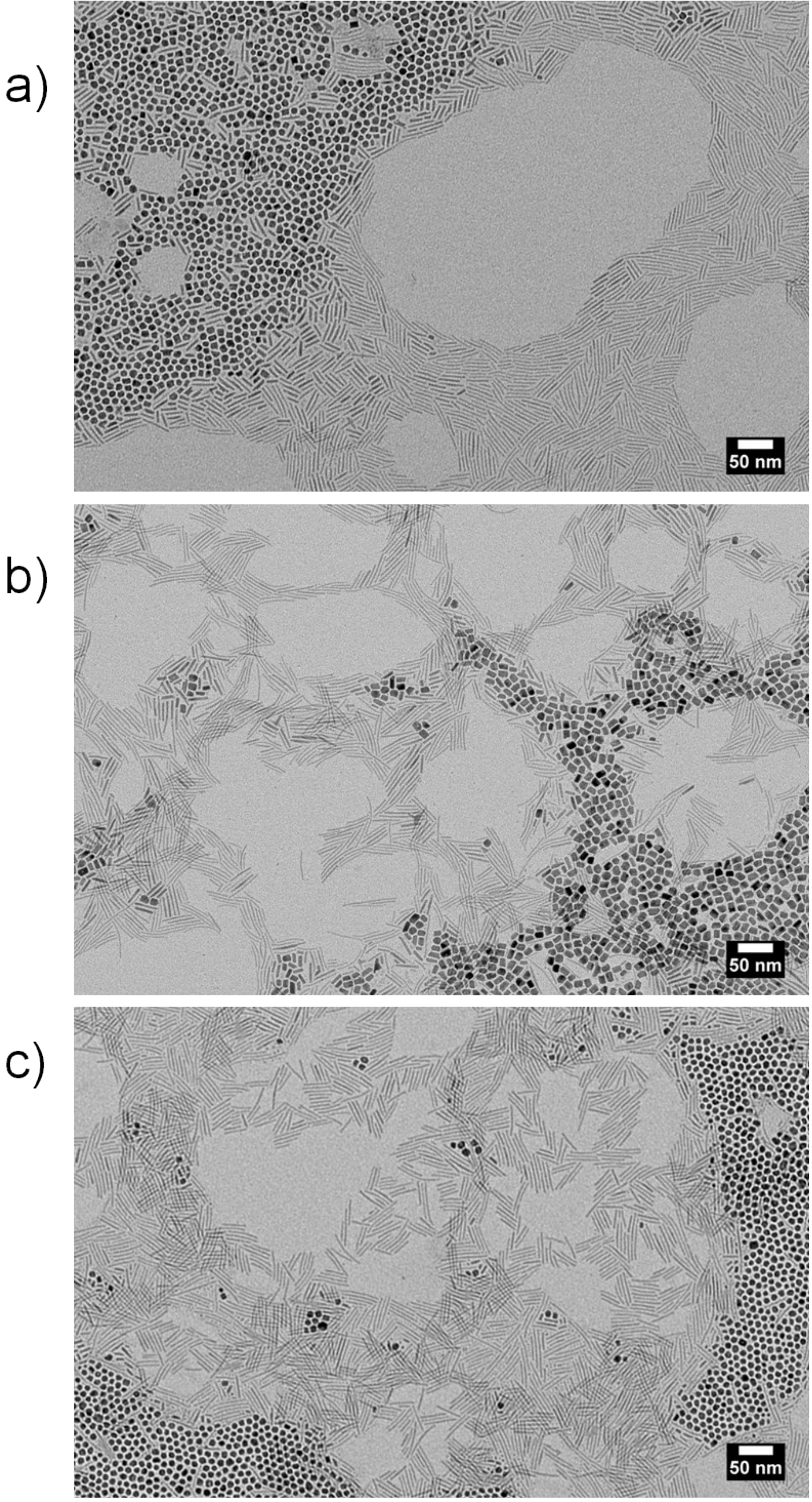


Fig. S9. Co NPs syntheses in 7 ml of tetradecane and 3 ml of OAm (ratio 7:3) with [$CoCl(PPh_3)_3$]. Co NPs were extracted after being washed with EtOH at 5h (a), 8h (b) and 15h (c).

TEM images of Co NRs with $[CoBr(PPh_3)_3]$ and $[CoI(PPh_3)_3]$

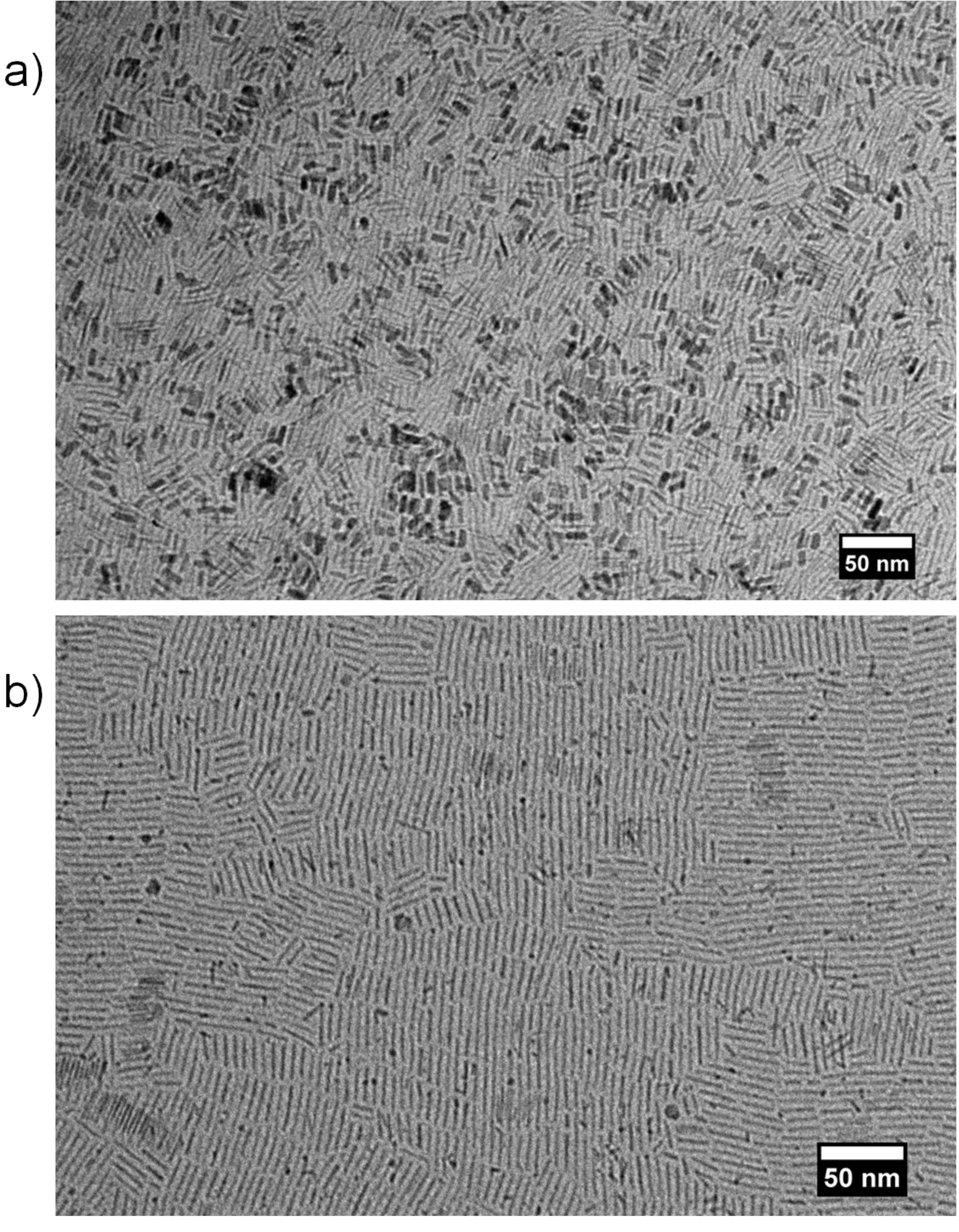


Fig. S10. TEM images of Co NRs in 10 mL of OAm with $[CoBr(PPh_3)_3]$ (a); $[CoI(PPh_3)_3]$ (b). NPs were extracted after being washed with EtOH at 10h $[CoBr(PPh_3)_3]$; 18h $[CoI(PPh_3)_3]$

E-TEM Characterization

E-TEM Images of the first steps of the Co NPs' dissolution in a real *in-situ* liquid cell (Protochips- Poseidon sample holder)

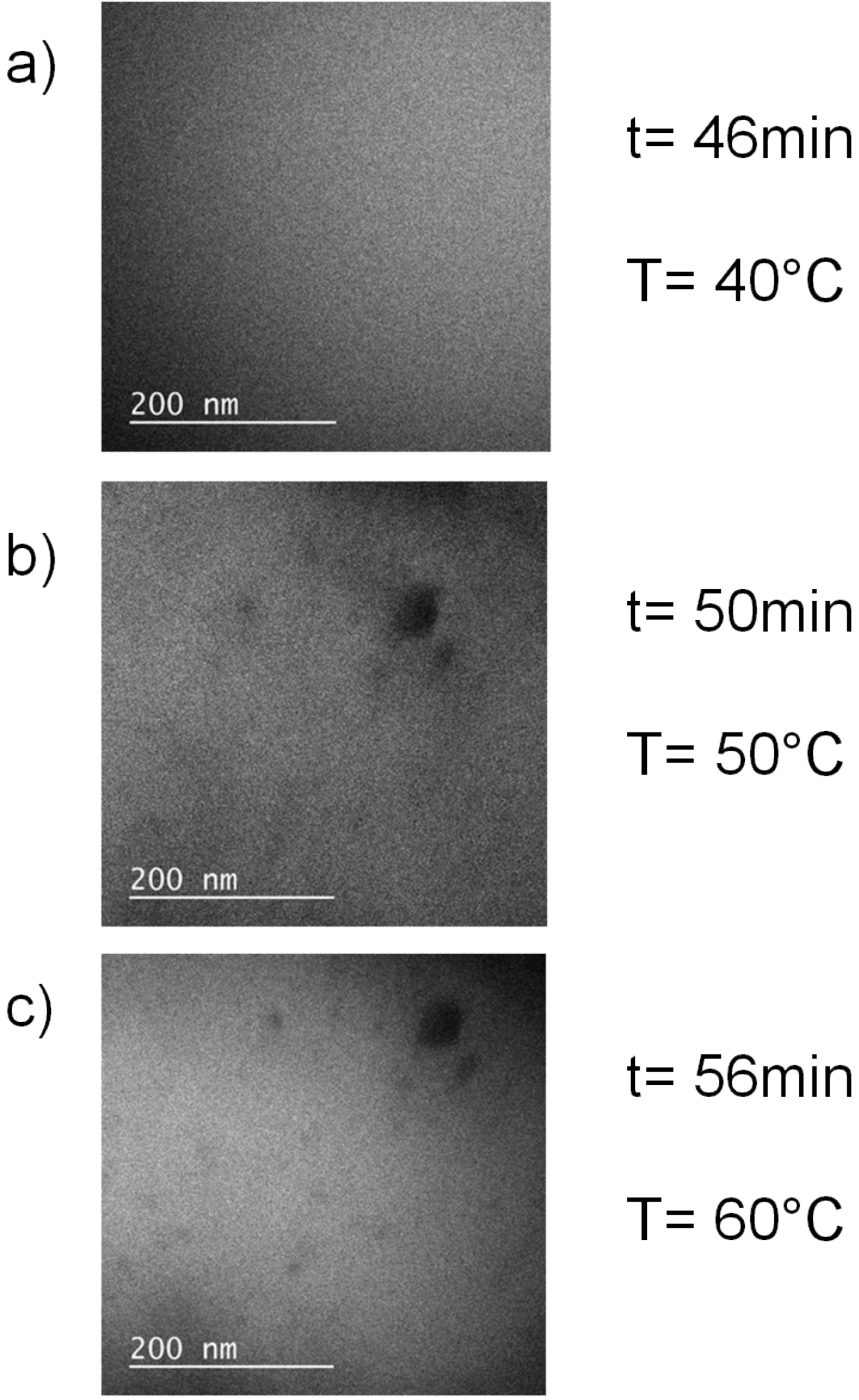


Fig. S11. E-TEM images of the Co precursor in OAm diluted 1/20 in toluene, in a liquid cell at 40°C (a) 50° C (b) 60°C (c).

E-TEM images of the nanospheres dissolution and the formation in-situ of cobalt nanorods.

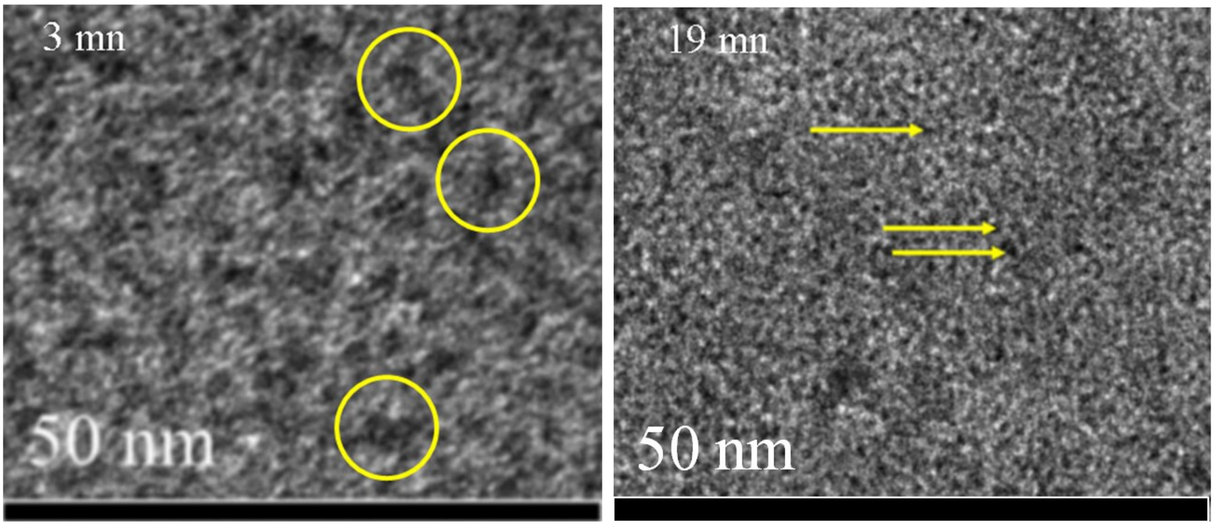


Fig. S12. E-TEM images of the nanospheres dissolution and the formation in-situ of cobalt nanorods, zoom at 3 min and 19 min.

NMR Characterization

NMR results of crude product in the catalytic reduction in H-tube

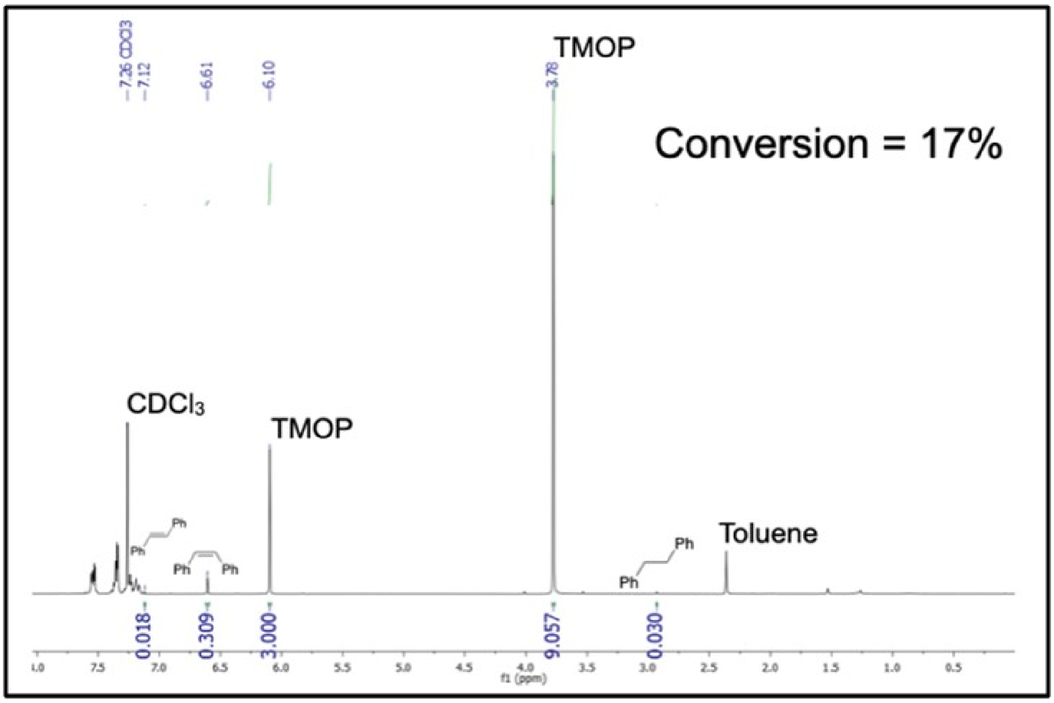


Fig. S13. Catalytic reduction in H-tube of diphenylacetylene by hydrogen released from OAm in presence of cobalt. NMR of crude products shows the presence of stilbene (TMOP = trimethoxyphenyl).

NMR results of the “white-pink” salt

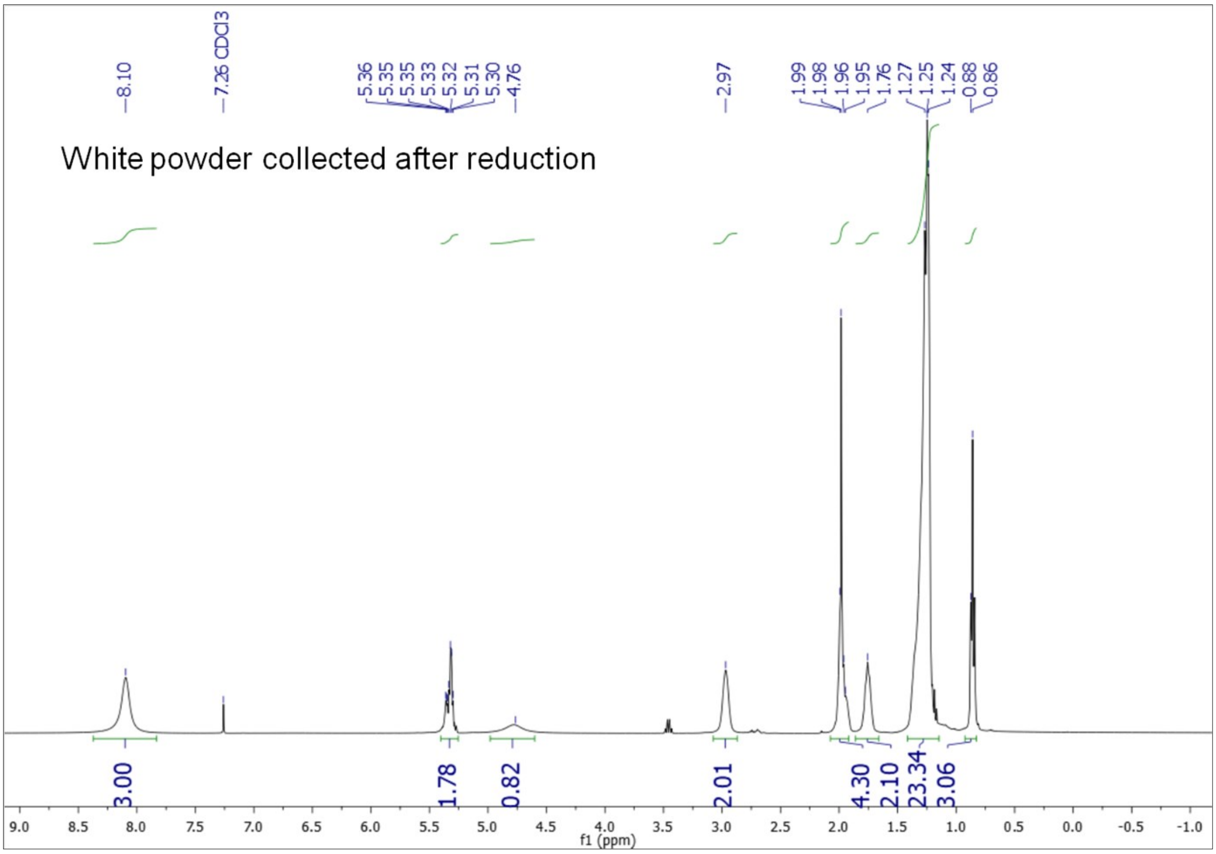


Fig. S14. Reduction of [$CoCl_2(PPh_3)_3$] by H_2 in OAm. NMR of the “white-pink” salt characteristic of an ammonium chloride.

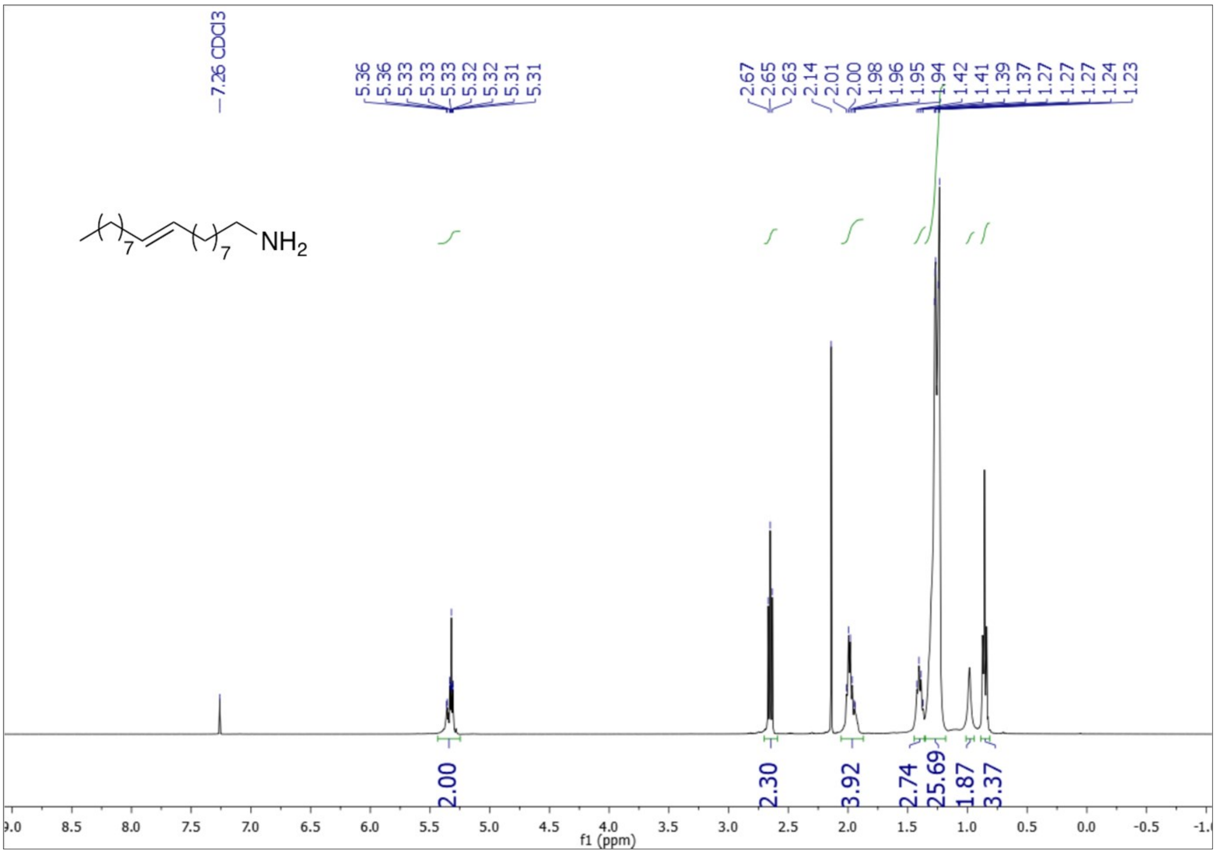


Fig. S15. NMR of OAm.

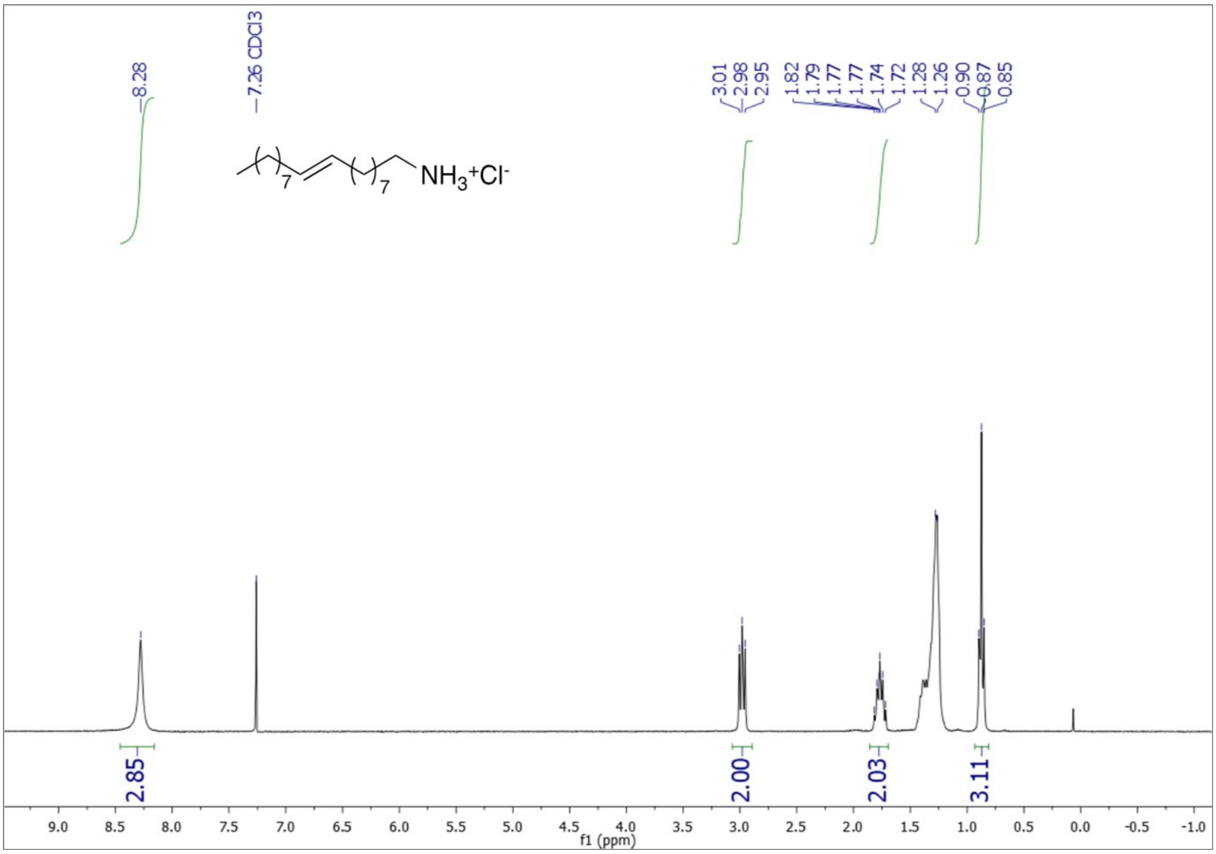
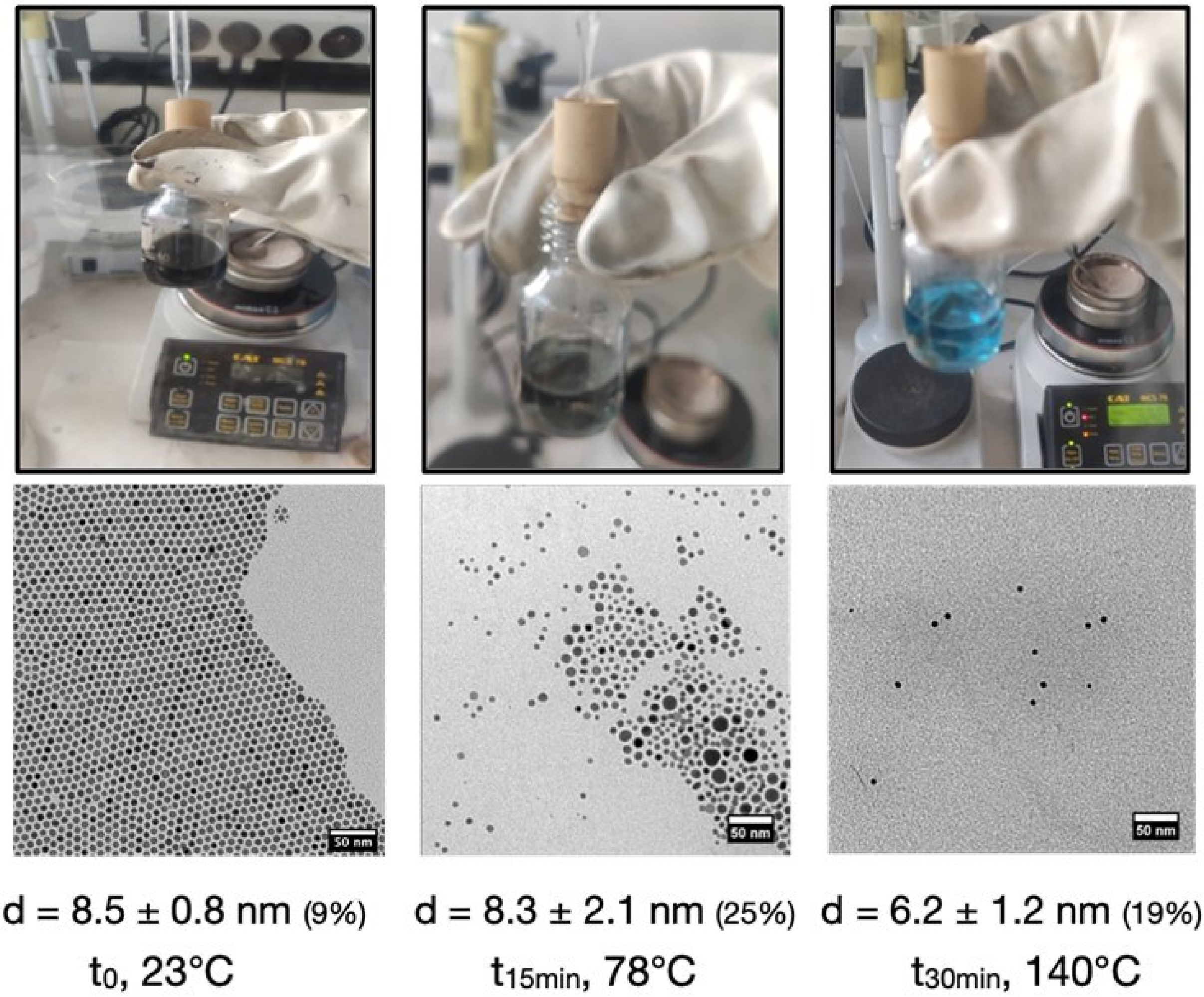


Fig. S16. NMR of OAm.HCl

Images corresponding to scheme (in the article)

Images of etching process



d = 8.5 ± 0.8 nm (9%) d = 8.3 ± 2.1 nm (25%) d = 6.2 ± 1.2 nm (19%)

t_0, 23°C t_{15min}, 78°C t_{30min}, 140°C

Fig. S17. Etching process overtime (30min) with a ramp of 230°C/h. The solution was a mixture of Co NPs, 10 mL of OAm, 4eq. of PPh_3 and 2eq. of OAm.HCl

Images of reduction process of cobalt (II) by dehydrogenation of OAm

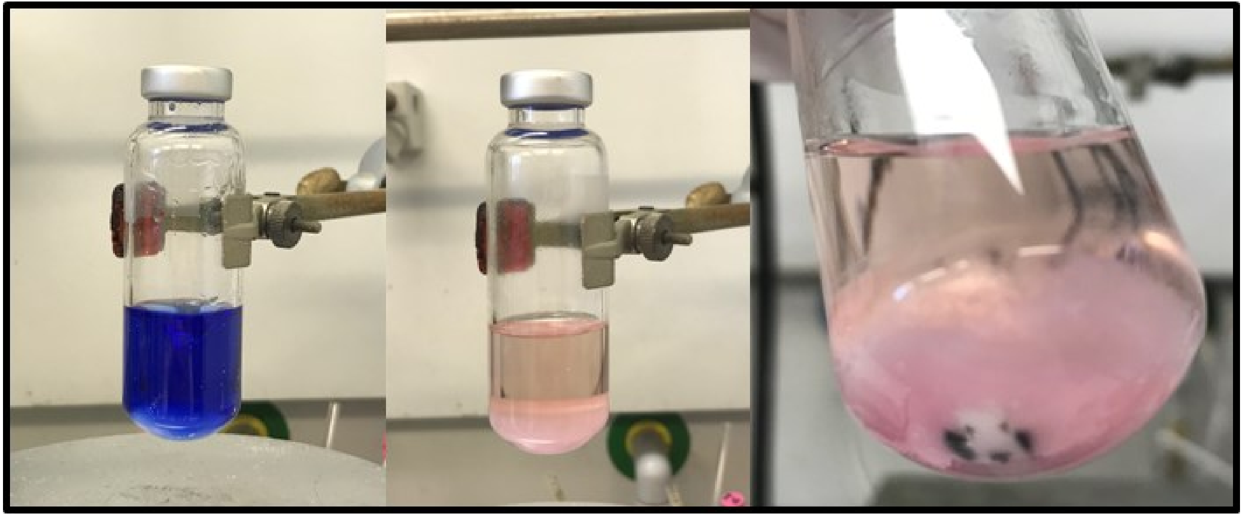


Fig. S18. Evolution of the solution's color under H_2 atmosphere before and after heating. Pictures of $[CoCl_2(PPh_3)_2]$ in OAm before and after heating at 190°C for 10 hours and zoom on the magnet cover by a magnetic black powder.

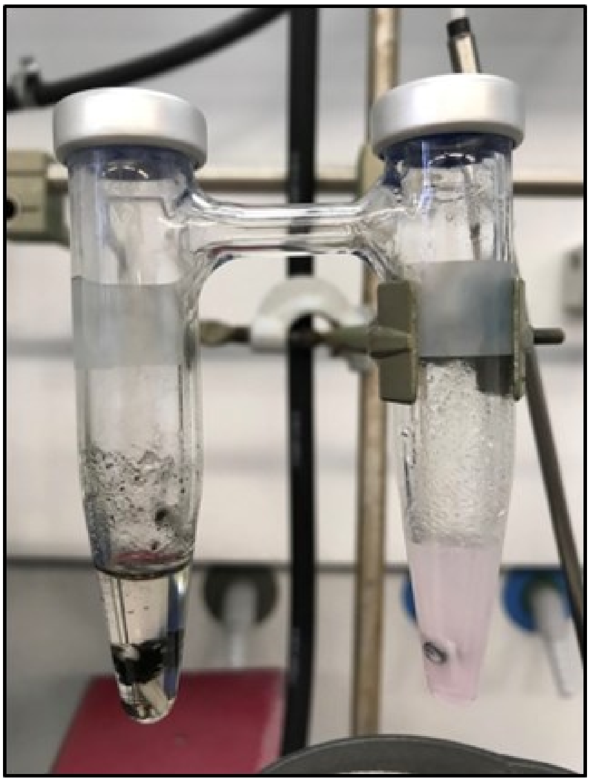


Fig. S19. Second proof of the reduction by H_2 of the cobalt (II) in cobalt (0). On one side Co NPs with ammonia borane complex on the other side $[CoCl_2(PPh_3)_2]$ with tetradecane which has been reduced after 10h at 190°C in cobalt (0).

Table of the blanks tests for the reduction of cobalt (II) [$CoCl_2(PPh_3)_2$] and the formation of Co NRs

Entry	Heating	Amine ($R\text{-}NH_2$)	Double bound (-C=C-)	Phosphine (PPh_3)	Co NPs	Results
1	X					Blue solution, no particle
2	X	X				Blue –purple solution, no particle
3	X		X			Biphasic solution (blue and colorless), no particle
4	X			X		Biphasic solution (blue and colorless), no particle
5	X	X	X			Blue-purple solution, no particle
6	X	X		X		Blue-purple solution, no particle
7	X		X	X		Biphasic solution (blue and colorless), no particle
8	X	X	X	X		Blue-purple solution, no particle
9	X				X	Blue supernatant, bulk
10	X			X	X	Biphasic supernatant (blue and colorless), bulk
11	X		X	X	X	Biphasic supernatant (blue and colorless), bulk
12	X	X			X	**Colorless supernatant, nanorods**
13	X	X	X		X	**Colorless supernatant, nanorods**
14		X	X		X	Blue-purple supernatant, spherical Co NPs

Table S2: Blanks tests for the reduction of cobalt (II) (from entry 1 to 8) and the formation of Co NRs (from entry 9 to 14).

For the reduction of cobalt (II): four parameters were tested as possible reducing agents: the heating (thermal degradation), the amine (from oleylamine), the double-bound (from oleylamine), the free phosphines (present in the media after the disproportionation).

Heating: 190°C

Amine ($R\text{-}NH_2$): Octadecylamine

Double bound (-C=C-): Octadecene

Amine + Double bound: Oleylamine

Phosphine $(PPh_3)_3$: 4 equivalents

If no Amine or Double Bound: Tetradecane

All these parameters were tested separately and collectively in the presence of $[CoCl_2(PPh_3)_2]$. None of them were able to reduce the cobalt (II).

For the formation of Co NRs: the same four parameters (same conditions) were tested in addition to the presence of Co NPs essential for the formation of Co NRs. It appears the presence of the heating (entry 14), the amine ($R\text{-}NH_2$) combined with the Co NPs resulted in the reduction of cobalt (II) (colorless supernatant) and the formation of Co NRs (entry 12 and 13).

Inter-lamellar distance calculation:

$$q = \frac{4\pi \times \sin\theta}{\lambda} \quad (1)$$

Eq. S1. Scattering vector

$$2d\sin\theta = n\lambda \quad (2)$$

Eq. S2. Bragg's Law

Scattering vector between two peaks: $q = 1.26\ \mathrm{nm}^{-1}$

Wave length $\lambda = 0.154$ nm

Inter-lamellar distance: $d = 4.99\ \mathrm{nm} \approx 5\ \mathrm{nm}$