One-step synthesis of metallic and metal oxide nanoparticles using amino-PEG oligomers as multi-purpose ligands: size and shape control, and quasi-universal solvent dispersibility[†]

Javier Rubio-Garcia,^{abc} Yannick Coppel,^{ab} Pierre Lecante,^d Christophe Mingotaud,^c Bruno Chaudret,^{ab} Fabienne Gauffre^{*c} and Myrtil L. Kahn^{*ab}

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A one-step and room temperature synthesis toward metallic and metal oxide nanoparticles soluble both in water and organic solvent is reported. This was achieved using amino-PEG oligomers that make it possible to control the size and shape of the nanoparticles.

Numerous methods for the preparation of nanoparticles (NPs) have been described in the literature. The solution synthesis of metallic NPs usually proceeds via the reduction of a precursor whereas metal oxide NPs necessitate an oxidation step. The various methods of synthesis performed in water present the advantage of yielding NPs dispersible in water including both metal oxide^{1,2} and metallic NPs.³ However, in most cases, large particles and broad size distributions are obtained due to ionic interaction between the growing nuclei. In addition, such approaches generally necessitate high temperature conditions.⁴ Fine control over size and shape is of tremendous importance for many applications because these parameters are critical to both physical and chemical properties of NPs. Therefore, one-step and room temperature (RT) synthetic procedures allowing access to NPs dispersible in a large range of solvents (in particular in water) are desirable, especially when considering formulation issues. In this context, it has been demonstrated that the organometallic solution synthesis is particularly effective in producing ultrasmall NPs (<10 nm) with a very well defined structure.^{5,6} This approach leads however to NPs which are only dispersible in non-polar solvents. As a consequence, strategies to produce water soluble NPs usually involve the transfer of the NPs from the organic solvent, either via ligand exchange with more hydrophilic capping molecules⁷⁻¹¹ or via the formation of interdigitated layers.¹²⁻¹⁵

Here we report a very simple RT synthesis procedure, yielding metallic or metal oxide NPs dispersible in almost any solvent, and especially in water, without the need of a

transfer step.¹⁶ To reach this goal, we took advantage of the versatility of organometallic chemistry to prepare either metallic or metal oxide NPs. We reasoned that the water-soluble poly (ethyleneglycol) (PEG) oligomers are also soluble in most non-polar solvents, and could be used as a ligand for this purpose. We targeted the commercially available amino-PEG oligomers, α -(2-ethylamine)-methoxy(ethyleneglycol) and poly (ethyleneglycol)bis (3-propylamine), referred to hereafter as ethylamine-PEG750 and bis-propylamine-PEG1500, respectively. The choice of an amine as the coordinating group was motivated by our previous observations that alkyl amine ligands lead to monocrystalline and well defined NPs.5,6 Indeed, in the presence of amino-PEG oligomers, metallic and metal oxide NPs were obtained in quantitative yields as powders which could readily be solubilized in many non-polar and polar solvents, including water.

In the present work, ZnO NPs were chosen as models for metal oxide materials. NPs were obtained via RT hydrolysis of the biscyclohexyl zinc precursor in the presence of either bis(propylamine)-PEG1500 (of mean molecular weight 1500 g mol⁻¹) or ethylamine-PEG750 (of mean molecular weight 750 g mol⁻¹) in a solvent (typically THF) (Scheme 1), using a procedure similar to the one previously reported by our group.¹⁷ The solution containing the Zn-precursor and the ligand was first prepared in a glove box under argon and then exposed to ambient moisture by opening the Schlenk tube. The amount of ligand was varied from $\rho_{\text{lig}} = 0.05$ to 2 (ratio of ligand versus zinc precursor). After solvent evaporation, the resulting powder could be dispersed in a large variety of polar and non-polar solvents including water, acetonitrile, ethanol, chloroform, tetrahydrofuran, and toluene (Fig. 1). In all cases colloidal suspensions were obtained with concentrations ranging from 1 to 3 g L^{-1} . Transmission Electron Microscopy (TEM) was used to observe the nanoparticles, measure their size and estimate their dispersion state.¹⁸ Fig. 1b presents typical TEM images of the ZnO NPs prepared using 1 equivalent of bis(propylamine)-PEG1500 and after dispersion



Scheme 1 Organometallic synthesis of metal oxide NPs using bispropylamine-PEG1500 molecule ($n \approx 30$) or ethylamine-PEG750 molecule ($n \approx 15$).

^a CNRS, LCC (Laboratoire de Chimie de Coordination), 205, route de Narbonne, F-31077 Toulouse, France. E-mail: myrtil.kahn@lcc-toulouse.fr; Fax: +33 5 6155 3003; Tel: +33 5 6133 3130

^b Université de Toulouse, UPS, INPT, LCC, F-31077 Toulouse, France

^c CNRS, IMRCP (Laboratoire des Interactions Moléculaires et Réactivités Chimiques et Photochimiques), 118 Route de Narbonne, F-31062 Toulouse, France.

E-mail: gauffre@chimie.ups-tlse.fr; Fax: +33.5 6155 8155; Tel: +33 5 6155 6143

^d CNRS, CEMES (Centre d'Elaboration de Matériaux et d'Etudes Structurales) 29, rue Jeanne Marvig, F-31055 Toulouse, France. Fax: +33 5 62257999; Tel: +33 5 62257851 Electronie supelement

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Fig. 1 (a) Photographs of dispersions of ZnO nanoparticles in various solvents under UV-light illumination ($\lambda = 365 \text{ nm}$, $\sim 3.40 \text{ eV}$). $\rho_{\text{lig}} = 1$, bis-propylamine-PEG1500; concentrations of the dispersions: 1 to 3 g L⁻¹. (b) TEM images of ZnO nanoparticles ($\rho_{\text{lig}} = 1$) left from a THF dispersion; right from a water dispersion. Histograms are given in the inset. The mean diameter is evaluated by fitting with a Gaussian curve. First and second values correspond to the center of the curve and to the standard deviation, respectively.

in THF (Fig. 1b₁) or in water (Fig. 1b₂). As can be seen, isotropic nanoparticles were obtained with a diameter of 4.0 ± 1.0 nm. Remarkably, no significant coalescence was observed in THF or in water. Similar results were obtained for all solvents investigated. Clearly, the size and shape were solvent independent. In water, the ZnO nanoparticles were chemically stable in the pH range 4–13 for more than one day.

The hydrodynamic diameters were measured by dynamic light scattering using a Malvern zetasizer "NanoZS" at a back-scattering angle of 173°. Data were interpreted using the Non Negative Least Square algorithm. Dispersions were sonicated for 30 minutes prior to measurements. The hydrodynamic diameters of ZnO NPs synthesized using bis-propylamine-PEG1500 ($\rho_{\text{lig}} = 1$) were 19 \pm 4 nm and 66 ± 8 nm in THF and water respectively. These values suggest partial aggregation of the particles and/or oligomers. The zeta potential of these ZnO NPs was measured using the "dip-in" cell system of the zetasizer. Values were relatively close to zero (-11.9 and -4.6 mV in THF and in water respectively), which shows that the system is stabilized by steric rather than electrostatic repulsion forces. Such negative values most likely resulted from hydroxy anions associated with the oligomer. Indeed, the medium is alkaline (pH \approx 9 in water) due to the presence of amino groups, and PEG chains are known to be strongly hydrated. This was confirmed by zeta potential measurements of the polymer alone (-10 mV and -10.5 mV in THF and water respectively).

The size of the NPs could be finely controlled by adjusting the amount of ligand introduced in the reaction medium. For instance, as the amount of bis(propylamine)-PEG1500 increases from $\rho_{\text{lig}} = 0.05$ to 2 equivalents, the mean size of the NPs decreases from 7.2 \pm 2.3 nm to 3.9 \pm 0.8 nm (S4, ESI†). Moreover, the size distribution becomes narrower as the amount of ligand increases. Shape control was achieved by modification of the experimental conditions (Fig. 2a and b). Isotropic, rod-like, and even triangular nanoparticles could be obtained. Typically, nanorods of *ca.* 20 \times 5 nm were formed when ethylamine-PEG750 oligomer was used instead of bis(propylamine)-PEG1500. Nano-triangles were formed in the presence of both ethylamine-PEG750 and acetic acid.¹⁹ Importantly, all samples were soluble in a wide range of solvent without the need for any surface modification.

Metallic NPs of Ru, Pt, and Pd were similarly obtained by reduction of an organometallic precursor under RT dihydrogen atmosphere in solution (S5, ESI[†]). Following the organometallic procedure previously reported by our group,⁶ Ru(COT)(COD), Pt₂(dba)₃, or Pd₂(dba)₃ was first dissolved in a solvent (e.g. THF) in the presence of the oligomer at -100 °C. The mixture was then allowed to reach RT. Then H₂ was supplied for 20 min at a pressure of 3 bars, and the mixture was left to react overnight at RT. After releasing the H₂, 30 mL of pentane was added in order to precipitate the nanoparticles (black powder). This solid was washed using 3 \times 30 mL of pentane. The powder formed stable colloidal solutions in various solvents (water, THF, toluene, acetonitrile, ethanol, chloroform). Very small isotropic Ru NPs of diameter ca. 1.1 ± 0.3 nm were obtained when ethylamine-PEG750 oligomer was used (Fig. 2c) while Ru NPs of 2.7 \pm 0.6 nm were obtained with bis(propylamine)-PEG1500 oligomer (Fig. 2d). Pd and Pt NPs were only obtained using a mixture of ethylamine-PEG750 and carboxymethyl-PEG3000 oligomers. Isotropic Pd NPs of 1.7 ± 0.6 nm were obtained (Fig. 2e) while worm-like Pt NPs were obtained under the same conditions (Fig. 2f). In all cases, TEM images show individually isolated NPs, indicating an absence of coalescence. All of the investigated solvents yielded similar results. The size and shape also remained unchanged regardless of the solvent.



Fig. 2 TEM images of ZnO NPs prepared in the presence of (a) ethylamine-PEG750 ($\rho_{\rm lig} = 0.5$) from a THF dispersion; (b) ethylamine-PEG750 ($\rho_{\rm lig} = 2$) and acetic acid from an anisole dispersion. TEM images of Ru NPs prepared in the presence of (c) ethylamine-PEG750 ($\rho_{\rm lig} = 1$) from a water dispersion; (d) bis(propylamine)-PEG1500 ($\rho_{\rm lig} = 1$) from a water dispersion. TEM images of Pd (e) and Pt (f) NPs prepared in the presence of ethylamine-PEG750 and carboxymethyl-PEG3000 ($\rho_{\rm lig} = 1$) from a water dispersion.

Interestingly, the dispersions of the metallic NPs were stable for months at RT.

Wide Angle X-ray Scattering (WAXS) measurements on samples sealed in Lindemann capillaries were performed in conditions allowing for RDF analysis (Mo wavelength, extended angular range, low background) in order to access the crystallographic characteristics of the NPs. For all of the samples, well defined diffraction peaks were observed, (S1, left, ESI†). The sharp peaks for $2\theta < 15^{\circ}$ are attributed to the crystalline ligand. This contribution (obtained in the same conditions from pure ligand) was subtracted prior to Fourier Transform (S1, right). For all samples, and especially for the less crystalline samples such as Ru, correspondence (in real space) of the experimental RDF spectrum with the calculated one is a clear indication of the metallic character of the NPs.

The interaction between oligomers and the NPs surface was investigated by NMR studies performed in deuterated water (S2, ESI[†]). For metallic as well as metal oxide NPs, the oligomer was observed to coordinate to the surface via the amine function. However, the strength of this interaction depends on the NPs surface. For metallic NPs the coordination of the oligomer via the amine function is strong whereas it is very weak for metal oxide NPs. In particular, the signals of the protons in the α and β -positions of the NH₂ function $(\delta^{-1}H 2.67 \text{ ppm (CH}_{2\alpha}) \text{ and } 3.46 \text{ ppm (CH}_{2\beta}), \text{ respectively) were}$ significantly affected by the oligomer interaction with the metallic surface. A complete disappearance of the $CH_{2\alpha}$ and CH₂₆ ¹H signals was even observed for Pt NPs. This is attributed to a locally restricted motion of the oligomer close to the NP surface and is associated with the presence of a Knight shift in the case of Pt NPs.²⁰ In the case of metal oxide NPs, the exchange rate between free and bound oligomers was rapid compared to the time scale of the NMR. In this case, the $CH_{2\alpha}$ and CH₂₆¹H signals were only weakly affected and only small shifts of the ¹H signals could be observed.

Coordination of the oligomers to the surface of metal oxide NPs was unambiguously confirmed by optical measurements (photoluminescence). Indeed, we have previously shown that coordination of amines to the ZnO NP surface leads to a specific emission in the blue region in addition to the usually observed emission in the yellow-green region.²¹ Emission and excitation spectra were recorded in THF and in water, yielding identical results in both solvents. Two excitation ranges can be defined (S3, ESI⁺): (i) excitation within the 290–360 nm range leads to a wide vellow emission band centered at ~ 590 nm: (ii) excitation within the 380-410 nm range leads to a blue emission band centered at 450 nm. A sharp band with low intensity was also observed. Its position depends on the excitation wavelength consistently with its Raman origin. A competition between the blue and yellow emissions takes place and interestingly, a selective excitation can be performed. Excitation within the band gap leads to yellow emission whereas at slightly higher energies a blue emission is observed. A white emission corresponding to the sum of the two can also be observed for an intermediate excitation

wavelength of 370 nm (S2a, ESI⁺). Similar results were obtained when ethylamine-PEG750 oligomer was used for the synthesis, also consistent with the coordination of this amine to the surface of the nano-objects.

In summary, metallic or metal oxide nanocrystals that are readily dispersible in water as well as in many other polar and non-polar solvents were obtained by a simple one-step RT procedure. This was achieved using organometallic reagents in combination with (amino)-PEG ligands. It was shown that such ligands can efficiently give access to well-defined crystalline nanoparticles with a narrow size distribution. It was possible to control the particle size and shape by varying the experimental conditions.

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