Nanocatalysts

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Highly Efficient Transition Metal Nanoparticle Catalysts in Aqueous Solutions

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Dedicated to Dr. Jean-René Hamon on the occasion of his 60th birthday

Abstract: *A ligand design is proposed for transition metal nanoparticle (TMNP) catalysts in aqueous solution. Thus, a tris(triazolyl)-polyethylene glycol (tris-trz-PEG) amphiphilic ligand,* ***2****, is used for the synthesis of very small TMNPs with Fe, Co, Ni, Cu, Ru, Pd, Ag, Pt, and Au. These TMNP-****2*** *catalysts were evaluated and compared for the model 4-nitrophenol reduction, and proved to be extremely efficient. High catalytic efficiencies involving the use of only a few ppm metal of PdNPs, RuNPs, and CuNPs were also exemplified in Suzuki–Miyaura, transfer hydrogenation, and click reactions, respectively.*

Since the seminal discoveries by Haruta[1] and Hutchings,[2] catalysis of chemical reactions by transition metal nanoparticles (TMNPs) has attracted considerable interest owing to its efficiency, greenness, convenient use, and improved understanding of reaction mechanisms.[3–9] The support and medium have been shown to play an essential role in TMNP catalysis, but relatively little attention has been paid to TMNP surface ligand design. Yet both TMNP formation in micelles or inverted micelles and catalysis therein are also strongly dependent on the stereoelectronic parameters of the stabilizing agents.[10–13]

Catalysis in water offers great advantages in terms of green chemistry, and has recently been actively investigated.[14–21] For instance, amphiphilic dendrimers are unimolecular micelles,[18–20] and this property has recently been exploited for catalysis in water with little as parts per million (ppm) amounts of molecular or TMNP catalysts.[21] The synthesis and use in catalysis of amphiphilic dendrimers as nanoreactors represents a very productive sophistication, but it is time-consuming, and one can conceptualize a related approach using simpler amphiphilic ligands.

Toward this goal, we suggest the design of weak, but multidentate bulky ligands that offer both easy displacement from TMNP surface by substrates for catalysis and sufficient TMNP stabilization. As a result, we report the amphiphilic tripodal ligand tris(1,2,3-triazolyl)-polyethylene glycol (tris-trz-PEG), **2**, that led to the synthesis of very small TMNPs with various transition metals (Fe, Co, Ni, Cu, Ru, Ag, Pt, Pd, and Au). These TMNP-**2** complexes are shown to be remarkably efficient catalysts of several major green reactions. First, 4-nitrophenol (4-NP) reduction by $NaBH_4$ in water was used as a model NP surface reaction to demonstrate the catalyst efficiency and compare all of these metals with one another. Then RuNP-catalyzed transfer hydrogenation of nitrobenzene with *i*-propanol as the hydrogen source in water/*i*-propanol, PdNP-catalyzed Suzuki–Miyaura cross-coupling reaction between bromobenzene and phenylboronic acid in water/EtOH, and CuNP-catalyzed azide–alkyne 1,3-cycloaddition (CuAAC, click) reaction in water were shown to work using extremely low amounts (down to a few ppm) of catalysts.

The synthesis of the tris-trz-PEG ligand **2** starts with the preparation of tris(1-benzyl-1*H*-1,2,3-triazol-4-yl)methanol,[22] **1** (Figure 1a). Three clicked trz rings of **1**, formed through CuAAC reactions,[23,24] are amphoteric π-electron-rich aromatics that are biocompatible and stable toward both oxidizing and reducing agents. They are neutral and weak ligands for TMNP core surfaces, but provide stabilization of TMNPs, owing to their bulk and compared to monodentate ligands.[25,26] This ligand is not water soluble, however, and the pursuit of green chemistry has led us to search catalysts in aqueous solution. To this end, a Williamson reaction was conducted between **1** and chlorinated PEG 2000 (mPEG2000-Cl) to form ligand **2** that contains both the tris-trz ligand and a water-solubilizing and biocompatible PEG chain. See the Supporting Information (Section 2) for the details.

The synthesis of the family of TMNP-**2** (with Fe, Co, Ni, Cu, Ru, Pd, Ag, Pt, and Au) was carried out in water at r.t. in the presence of the ligand **2** by $NaBH_4$ reduction of the transition metal salts followed by dialysis (Figure 1b; Supporting Information, Section 3). Both the trz groups of the

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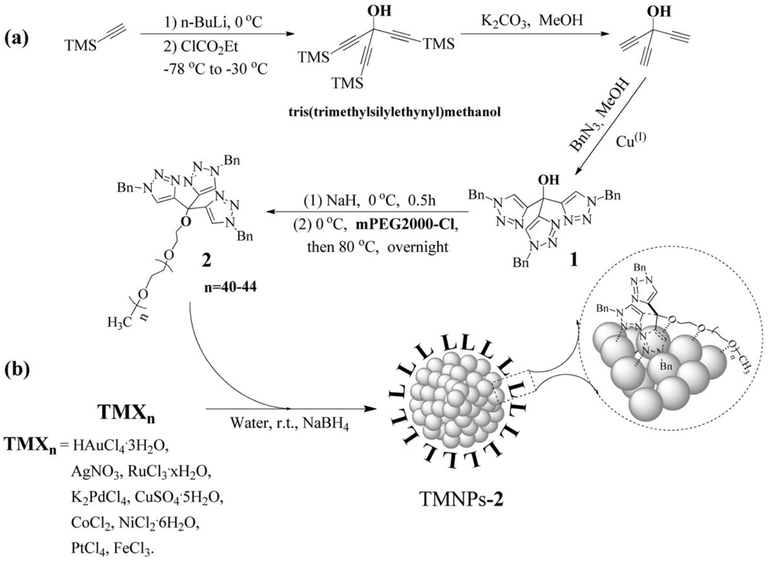


Figure 1. a) Synthesis of the amphiphilic ligand **2**. b) Synthesis of the TMNP-**2**.

tris-trz ligand and the PEG 2000 polymer are acting as weak ligands for the TMNP-**2**, whereby the synergy between weak, but multidentate, TMNP surface coordination and the overall large bulk permit the stabilization of these TMNPs (Figure 1b). Although the neutral nitrogen ligands are known to be better ligands than the neutral oxygen ligands, the electronic delocalization within the trz ligands very much weakens the nitrogen donor ability, which should favor catalytic reactions by easy ligand substitution by substrates for surface catalysis. The thermal stability of the TMNP-**2** in water is ascertained by the lack of aggregation throughout catalytic experiments, even upon heating under inert atmosphere (see below).

For instance, with AuNP-**2**, refluxing the aqueous solution for 5 hours did not provoke aggregation or any change of the SPB at 515 nm (Figure S15). Moreover, although the large class of AuNPs with thiolate ligands contain Au^{I} surface atoms, in the present case the X-ray photoelectron spectroscopy (XPS) signals at 84.05 eV for Au 4f$_{7/2}$ of AuNP-2 clearly show the presence of only Au^{0} surface atoms (Figure 2a and S16). We selected the 4-NP reduction to 4-AP by NaBH$_4$ in water catalyzed by TMNPs [Eq. (1)] as a standard reaction that can be used to evaluate the potential of the new ligand **2** to promote catalytic activity at the surface of TMNP-**2**. This homogeneous reaction is simple, without side paths, and easily monitored through UV/Vis spectroscopy by the decrease of the strong adsorption of the 4-NP anion at 400 nm.[27–29] The Ballauff group has shown that the mechanism (although unknown) involves rearrangement of the substrates 4-NP and NaBH$_4$ at the AuNP surface according to the Langmuir–Hinshelwood (LH) kinetic model, that is, the diffusion of the reactants is fast compared to the rate-limiting substrate rearrangement at the AuNP surface.[27]

The AuNP-**2** displays a surface plasmon band (SPB) at 515 nm in the UV/Vis spectrum, and a core size of 2.9 ± 0.3 nm in TEM (Table 1; Supporting Information). First, the 4-NP reduction in water catalyzed by AuNP-**2** was conducted [Eq. (1)], and the reaction rates show that the AuNP-**2** is one of the most efficient catalysts known ($k_{app} = 4.37 \times 10^{-2}\,s^{-1}$), compared with other catalysts from the literature (Supporting Information, Table S2). In addition, no induction times are found for the AuNP-**2**, although the latter was observed in previous studies of thiolate-AuNPs and citrate-AuNPs.[30] The very high reaction rates observed here, and the absence of induction time, reveal the successful design of AuNP-**2** as very efficient catalysts, as expected from the weak bonding ability of the trz- and PEG-coordination to AuNPs. The catalyst AuNP-**2** was recycled five times with reaction rates that decreased only overall by less than 20 %, showing good stereoelectronic stabilization by the ligand **2**, although the catalyst undergoes Ostwald ripening illustrated by the core size increase and slight variations by a few nm in the SPB. This structural change is due to catalysis at the AuNP-**2** surface, introducing the 4-AP product as a ligand. Precipitation is never observed, however. Finally, we compared 4-NP reduction catalyzed by AuNP-**2** and AuNP-**3**, the latter being stabilized by the ligand trz-PEG 2000, **3**, which contains a single trz ligand (Figure S10).

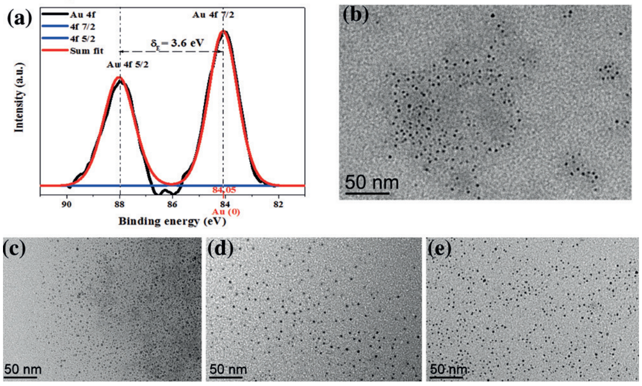
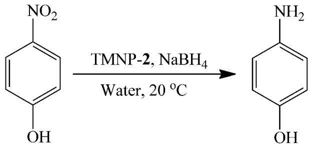


Figure 2. Characterization of TMNP-**2**. a) X-ray photoelectron spectroscopy (XPS) of Au 4f. Typical TEM images of the as-synthesized: b) AuNPs, c) PdNPs, d) AgNPs, and e) PtNPs. For additional characterization of TMNP-**2**, see the Supporting Information, Section 3.

In this way, the goal was to examine the influence of the multiplicity of the mono- versus tris-trz ligands containing the same PEG tail. The results indicate that the catalysis of 4-NP was significantly faster with AuNP-**2** ($k_1 = 0.410\,L\,s^{-1}\,m^{-2}$) than with AuNP-**3** ($k_1 = 0.253\,L\,s^{-1}\,m^{-2}$), showing the positive influence on catalysis of the tris-trz ligand bulk in **2** near the AuNP-**2** surface.

We then extended the use of **2** to the synthesis of TMNP-**2** with both cheap, abundant metals (Fe, Co, Ni, and Cu), and some other second- and third-row noble transition metals (Ru, Pd, Pt, and Ag) in the same manner as for the above-mentioned preparation of AuNP-**2** (Figure 1b). Interestingly, most of the TMNPs were formed with **2** in their nanocluster size (< 2 nm), except the CoNPs and AgNPs which were

Table 1: 4-NP reduction by $NaBH_4$ catalyzed by TMNP-**2** in water at 20 °C.



(1)

TMNP-**2**	Amount[a] [mol %]	D_{core}[b] [nm]	t_0[c] [s]	k_{app}[d] [10^{-3} s^{-1}]	k_1[e] [$L s^{-1} m^{-2}$]
FeNPs	2	1.3	780	1.88	1.21×10^{-3}
CoNPs	2	2.1	420	1.47	1.57×10^{-3}
NiNPs	2	1.6	720	0.30	2.69×10^{-4}
CuNPs	2	1.4	940	2.48	1.75×10^{-3}
AgNPs	2	2.2	520	7.85	6.07×10^{-3}
PtNPs	0.2	1.7	0	1.86	1.17×10^{-2}
RuNPs	0.2	1.0	0	3.15	1.26×10^{-2}
PdNPs	0.2	1.5	0	24.80	0.137
AuNPs	0.2	2.9	0	43.70	0.410

[a] Amount of TMNP-**2** used in the catalyzed 4-NP reduction. $NaBH_4$ is in excess. [b] Core size (TEM) of the TMNP-**2**. [c] Induction time. [d] Rate constant. [e] Surface-independent rate constant.

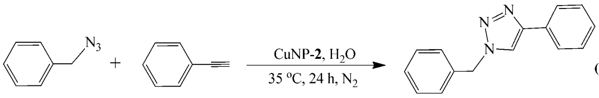
slightly larger than 2 nm (Table 1). This small size is advantageous for catalysis because the majority of atoms (54–70 %) are located on the TMNP surface for these metals (Fe, Ni, Cu, Ru, Pd, and Pt), forming monodispersed TMNP-**2** cores with diameters smaller than 2 nm (Figure 2b–e; Supporting Information, Section 3). Thus, the catalytic properties of these TMNP-**2** were also evaluated for the model 4-NP reduction with $NaBH_4$ [Eq. (1)].

For the group of first-row NPs, the induction time was observed in all the cases, and these TMNP-**2** exhibited the reaction rate order of Cu > Co > Fe > Ni in k_1 ($k_1 = k_{app}/S$, S being the NP core surface area).[27,28] Interestingly, no SPB of CuNP-**2** was observed, whereas a SPB at 590 nm was observed for large CuNPs in the absence of **2** (Figure S18). Indeed, the SPB is absent in the UV/Vis spectra of the very small nanoclusters, in which the molecular structure dominates.[31,32] CuNP-**2**, with its small size (1.4 nm), presented no SPB, and showed a reaction rate of $k_1 = 1.75\times10^{-3}$ $L s^{-1} m^{-2}$.

Other noble metal NP-**2** (Au, Pd, and Pt) catalyzed the 4-NP reduction very well, using only 0.2 mol % catalyst, and no induction time was observed. In this category, the reaction rate k_1 decreased with the order of Au > Pd > Pt > Ag. In the group 11 (Cu, Ag, and Au), from the first to the third row of transition metals, the induction time decreases, and the reaction rates greatly increase, which is best taken into account by the increased facility of oxidative addition in the catalytic mechanism for heavier late transition metals (Table 1). For RuNPs, exceptionally small sizes (1 nm) and remarkably high reaction rate constants were observed ($k_1 = 1.26\times10^{-2}$ $L s^{-1} m^{-2}$), ranking third best among these TMNP-**2**. Altogether, the tris-trz-PEG amphiphilic ligand **2** stabilized very small, monodispersed TMNP-**2** with high efficiencies, as shown in the comprehensive comparisons of the recent literature for reaction rate constants of TMNP-catalyzed 4-NP reduction reactions with various stabilizers (Table S3). Note that, although the first-row transition metal NP-**2** complexes exhibited high efficiencies in the 4-NP reduction when compared to other reported catalysts, their catalytic activities were still much lower than those of the noble metal NP-**2**.

For further catalytic investigations, we then selected three of the most efficient TMNP-**2** (Cu, Pd, and Ru), AuNP-2 having already been shown to exhibit excellent catalytic activity for 4-NP reduction (see above).

CuAAC[23,24] is well established as one of the most useful reactions in organic synthesis, materials science, and biomedical sciences. Recently, it has also been shown that CuNPs are active catalysts for this reaction.[33–38] CuNP-**2** was tested here as a catalyst for AAC between benzyl azide and phenylacetylene [Eq. (2)], and found to be highly efficient. This reaction was quantitatively achieved at 35 °C for 24 h using only 20 ppm of Cu from CuNP-**2**, leading to an exceptional TON of 28 000 and TOF of 1170 h^{-1} (Table S4). This is one of the best results ever obtained using CuNP catalysts.



(2)

For the investigation of the actually active species, X-ray photoelectron spectroscopy (XPS) of CuNPs was conducted (Figure 3). The main Cu peak, Cu $2p_{3/2}$, is found at binding energy (BE) of 932.6 eV (Figure 3a). The very weak satellite at around 945 eV gives the first indication of Cu^I and the absence of Cu^{2+}. Other indications for assignment to Cu^I are on one hand the Cu $2p_{3/2}$ peak at a relatively high FWHM compared to the C 1 s peaks (2.3 eV vs. 1.4 eV; Figure 3a and S45), and on the other hand the modified Auger parameter calculated from the Cu LMM (Figure 3b) that is assigned to Cu^I (Supporting Information, Section 5). All of these data showed that the catalyst was in its classic Cu^I state.[23,24] It is unavoidable that the CuNPs surface is oxidized by molecular oxygen from the air, and the active Cu^I species is thus formed in the native oxide layer on the Cu surface through comproportionation of Cu^0 and Cu^{II}, even if caution is taken to remove air. Recycling experiments using 100 pm of Cu from CuNP-**2** provided yields larger than 80 % during at least four successive recycling experiments, showing the good stability of the catalyst CuNP-**2**.

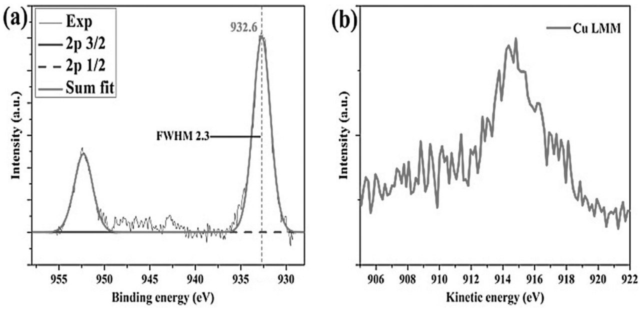
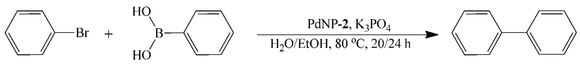


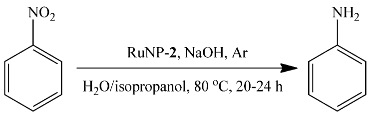
Figure 3. a) X-ray photoelectron spectroscopy of Cu 2p. b) Cu LMM Auger spectra.

The palladium-catalyzed Suzuki–Miyaura reaction is one of the common cross carbon–carbon coupling reactions.[39–42] Thus, catalysis of this reaction with ppm amounts of Pd is an ongoing challenge,[43,44] and only a few works are known to use this approach.[21,45–47] PdNPs are a valuable option, because toxic ligands that are often employed in efficient Pd catalysis are avoided with PdNP catalysts. The 1.5 nm core-sized PdNP-**2** with Pd^0 surface (from UV/Vis spectroscopy; Figure S20) catalyzed the Suzuki–Miyaura reaction between bromobenzene and phenylboronic acid using down to 10 ppm Pd per mol substrate [Eq. (3)], reaching a TON of 89000 and a TOF of $3700\,h^{-1}$ in 24 h at 80 °C in water/EtOH mixture (Supporting Information, Section 6). After the reaction, no aggregation of PdNPs was observed, indicating the very good thermal stability of the PdNP-**2**. In addition, recycling the PdNP-**2** catalyst in 0.1 mol % for this reaction gave yields of 87 % or above up to the 5th successive recycling run, with only a slight increase of the PdNP-**2** core size from 1.5 to 1.8 nm (Figure S54) without any aggregation.



(3)

Another challenging example is the catalysis of transfer hydrogenation (TH). TH refers to the addition of hydrogen to a molecule using a non-H_2 hydrogen source (such as isopropanol). It is a convenient, powerful, and green method to access various hydrogenated compounds.[48,49]



(4)

The UV/Vis spectrum of the RuNP-**2** confirms reduction to the Ru^0 surface following $NaBH_4$ reduction of $RuCl_3{\cdot}x\,H_2O$ (Figure S21). We found that the RuNP-**2** efficiently catalyzed TH of nitrobenzene using H_2O/isopropanol as the solvent at 80 °C in the presence of the base with only 0.01 mol % of catalyst at 80 °C for 24 h [Eq. (4)], leading to a TON of 2300 and TOF of $96\,h^{-1}$ (Table S5). Recycling this catalyst with 0.1 mol % RuNP-**2** provided a product yield of 85 % or more up to the 3rd successive recycling run.

In summary, ligand design for nanoparticle catalysis with very weak but multidentate N and O ligands has been shown to apply to the stabilization and remarkable catalytic efficiency of very small, water-soluble TMNPs-**2**. The favorable effect of the tris-trz ligand **2** over the less bulky, simple mono-trz ligand **3** is illustrated by the increased reaction rate of AuNP-catalyzed 4-NP reduction observed with **2** compared to **3**. The success of the ligand design involving **2** was exemplified with the catalysis by TMNP-**2** of various major reactions that were conducted in water or aqueous media. This engineering efficiently applies to the first row transition metals, as shown with click chemistry and the reduction of the 4-nitrophenol pollutants to useful 4-aminophenol dyes. It also applies to the noble transition metals with the use of only ppm amounts of TMNP-**2** catalysts for transfer hydrogenation of nitrobenzene, reduction of 4-NP, and cross carbon–carbon coupling.

The recyclability studies were conducted using a biphasic organic/aqueous separation of products and subsequent addition of new reactants, which is a potential means to reuse the catalyst in a continuous flow-type arrangement. Many other reactions should benefit from this simple and general concept, operating under green conditions with ppm amounts of TMNP catalyst and in the absence of toxic ligands. So far, very few studies have demonstrated the possibility using only ppm amounts of metal, responding to the industrial limit of a maximum of 5 ppm of residual metal in products,[21,45–47] and this new concept should enhance trends towards this goal.

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