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Short communication

Asymmetric hydrogenation of ethyl pyruvate over aqueous dispersed Pt nanoparticles stabilized by a cinchonidine-functionalized β-cyclodextrin

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ABSTRACT

Cinchonidine-functionalized β-cyclodextrin was used as stabilizing agent for platinum nanoparticles dispersed in water, but also as chiral modifier for the asymmetric hydrogenation of ethyl pyruvate at 30 °C under 40 bar of hydrogen. This functionalized cyclodextrin allowed getting more stable, more catalytically active and also more enantioselective Pt nanoparticles compared to control catalytic systems. NMR and MALDI-MS analyses clearly showed the reduction of the vinyl group of the cinchonidine graft during the nanoparticles preparation. Under hydrogen pressure, the hydrogenation of the quinolinic moiety was also proven and can be responsible for the difficulties encountered during the recycling study.

1. Introduction

Since the second half of the 20th century, asymmetric hydrogenation has always been a challenging research area [1,2]. Most of the efficient catalytic systems are based on the use of molecular metal catalysts with well-defined chiral ligands [3] or supported metal catalysts in the presence of a chiral modifier [4,5], which creates a crucial enantiodifferentiating interaction between the substrate and the chiral modifier on the metallic surface. Among the numerous reviews concerning enantioselective hydrogenation, the most studied chiral modifiers are cinchona derived compounds with good to excellent enantiomeric excesses (*ee*) for metal-based catalytic systems [5]. Despite a large number of publications, the clear identification of the key parameters to get the highest *ee* seems to be difficult. Different parameters such as the solvent, the substrate, the metal - support interactions or the metal source can deeply influence the catalytic results in terms of enantioselectivity.

Solvent dispersed metal nanoparticles (NPs) have received considerable attention for the twenty past years especially in catalysis [6], because they provide a high surface area of catalytically active metal thanks to a large fraction of surface-exposed metal atoms and a high number of edges and defects. While providing long-term stability of the dispersed particles, the choice of a capping agent is critical as it helps to control the size and shape of the particles as well as the accessibility of active surface sites to the reactants. Moreover, in the case of asymmetric hydrogenation, a critical condition is to find the most advantageous interactions between the metal NP, the chiral modifier and the substrate.

To the best of our knowledge, only few metal nanocatalysts modified by chiral ligands and dispersed in organic or aqueous media have been described in the hydrogenation of prochiral molecules [7–12]. In aqueous medium, Roucoux group synthesized platinum nanoparticles stabilized by *N*,*N*-dimethyl-*N*-hexadecyl-*N*-(2-hydroxyethyl) ammonium chloride ($HEA_{16}Cl$) [9], known as an efficient metal NPs stabilizer [13]. This colloidal suspension was evaluated in the ethyl pyruvate hydrogenation in the presence of cinchonidine and led to high enantiomeric excesses. To constrain the different parts of the catalyst to be close to each other, Roucoux has also described a series of optically active amphiphilic compounds as efficient stabilizers of rhodium NPs in water but low *ee* were obtained [14,15].

Among the water soluble capping agents, cyclodextrins [16], that are cyclic oligosaccharides composed of six (α-), seven (β-) or eight (γ-) α-D-glucopyranose units connected by α-(1,4)-linkage have proven to be effective stabilizers of metal NPs in water. They have also demonstrated their potential for catalytic applications in aqueous phase, such as for the hydrogenation of petro and biosourced substrates [17,18]. In

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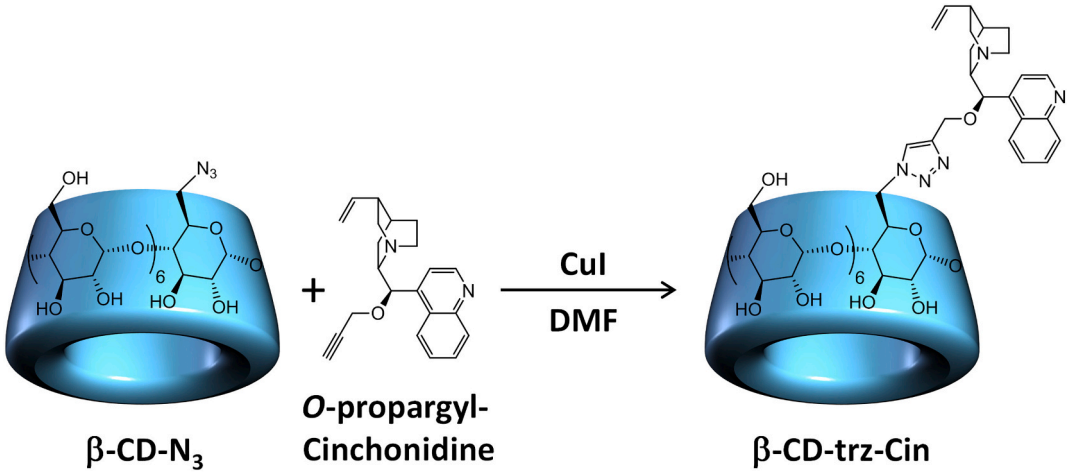


Fig. 1. Synthesis of **β**-CD-trz-Cin by click chemistry between azido-**β**-CD and propargyl cinchonidine.

particular, amino acid-functionalized cyclodextrins were used as chiral stabilizers of ruthenium nanoparticles dispersed in water for the asymmetric hydrogenation of methyl-2-acetamidoacrylate, ethyl pyruvate, acetophenone and *m*-methylanisole [19]. Promising results were obtained in terms of catalytic activity but no enantioselectivity was noticed.

Considering the best results with supported catalysts in the presence of a chiral modifier, a cinchonidine-functionalized cyclodextrin used as both NP stabilizer and chiral modifier was considered. We reported that cinchonidine-functionalized-β-cyclodextrin (β-CD-trz-Cin) could be used for the platinum nanoparticles synthesis in aqueous medium using sodium borohydride as reducing agent. Then, the catalytic activity of these obtained Pt NPs was evaluated in the hydrogenation of ethyl pyruvate at 30 °C under 40 bar of hydrogen. The recyclability study of these Pt NPs was also considered. Finally, NMR and MALDI-MS analyses were performed to understand this catalytic system.

2. Experimental section

2.1. Chemicals and reagents

Native β-cyclodextrin, abbreviated as β-CD, was kindly supplied by Roquette Frères (Lestrem, France). All chemicals were purchased from Aldrich Chemicals or Acros Organics and were used without further purification. Chloroplatinic acid hexahydrate (38–40 wt% Pt) was supplied by Strem Chemicals.

2.2. Characterization techniques

Transmission Electron Microscopy (TEM) was performed on a Tecnai microscope (200 kV). A drop of the colloidal suspension was deposited onto a carbon coated copper grid. Metal particle size distributions have been determined from the measurement of around 200 particles found in arbitrarily chosen area of the images using ImageJ software. NMR spectra were recorded at 298 K on a Bruker Avance III HD 300 NanoBay spectrometer equipped with a 5 mm broadband probe BBFO with *Z*-gradients, operating at 7.05 T field strength at 300 MHz for ^{1}H nuclei. DMSO-D_6 (99.80%isotopic purity) and D_2O (99.92% isotopic purity) were purchased from Euriso-Top. Mass spectra were recorded on a MALDI-TOF/TOF Bruker Daltonics Ultraflex II in positive reflectron mode with 2,5-DHB as matrix.

2.3. Synthesis of water dispersed Pt NPs stabilized by cinchonidine-functionalized β-CD

In a typical experiment, the colloidal suspension was prepared as follows at ambient temperature. 12 mg of β-CD-trz-Cin (8 μmol) were dissolved in 5 mL of HPLC water. Besides this solution, 4 mg of H_2PtCl_6 hexahydrate (8 μmol) were diluted in 3 mL of water and were added to the previous solution. The mixture was kept under constant stirring at room temperature for 30 min before the quick addition of 1.5 mg of sodium borohydride (0.04 mmol) dispersed in 4 mL of HPLC water. The color of the reaction medium changes upon addition of $NaBH_4$ from yellow to dark brown due to the reduction of Pt (IV). The resulting colloidal dispersion was visually stable as shown by the absence of observed metal sedimentation after 18 h of stirring at room temperature.

2.4. Catalytic test

All hydrogenation experiments have been performed using a Parker-Autoclave Engineers stainless steel autoclave containing a glass vessel which was charged with 6 mL of standard platinum colloidal suspension and 232 mg of ethyl pyruvate (2 mmol, 500 eq.). Hydrogen was fed to the system at constant pressure up to 40 bar. The mixture was heated up to 30 °C with a thermostated oil bath and stirred at 1000 rpm. The reaction was monitored by analyzing an aliquot of the reaction mixture after 1.5 h of reaction with a Shimadzu GC-2010 Plus gas chromatograph, equipped with a capillary column in polyethylene glycol (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector using decane as an external standard. Enantiomeric excesses were determined with a Perkin Elmer Clarus 590 gas chromatograph, equipped with a capillary column CHIRALDEX β-CD (30 m × 0.25 mm × 0.12 μm) and a flame ionization detector.

2.5. Recyclability study

At the end of the reaction, all organic compounds were extracted using chloroform. After decantation and chloroform removal, the aqueous phase containing the catalyst was reused for another run by reloading with ethyl pyruvate and fed with hydrogen.

3. Results and discussion

The synthesis of β-CD-trz-Cin has already been described in a previous publication [20]. Briefly, this compound was obtained by copper catalyzed coupling between 6^{I}-azido-6^{I}-deoxy-β-CD (β-CD-N_3) and *O*-propargyl cinchonidine in DMF (Fig. 1).

Concerning the synthesis of the platinum NPs, the procedure is very similar to those previously reported by our team [21,22]. In short, the synthesis involves a one-step reduction of the platinum (IV) salt, in the presence of controlled amounts of β-CD-trz-Cin and an excess of sodium borohydride, in water and at room temperature. Contrary to our

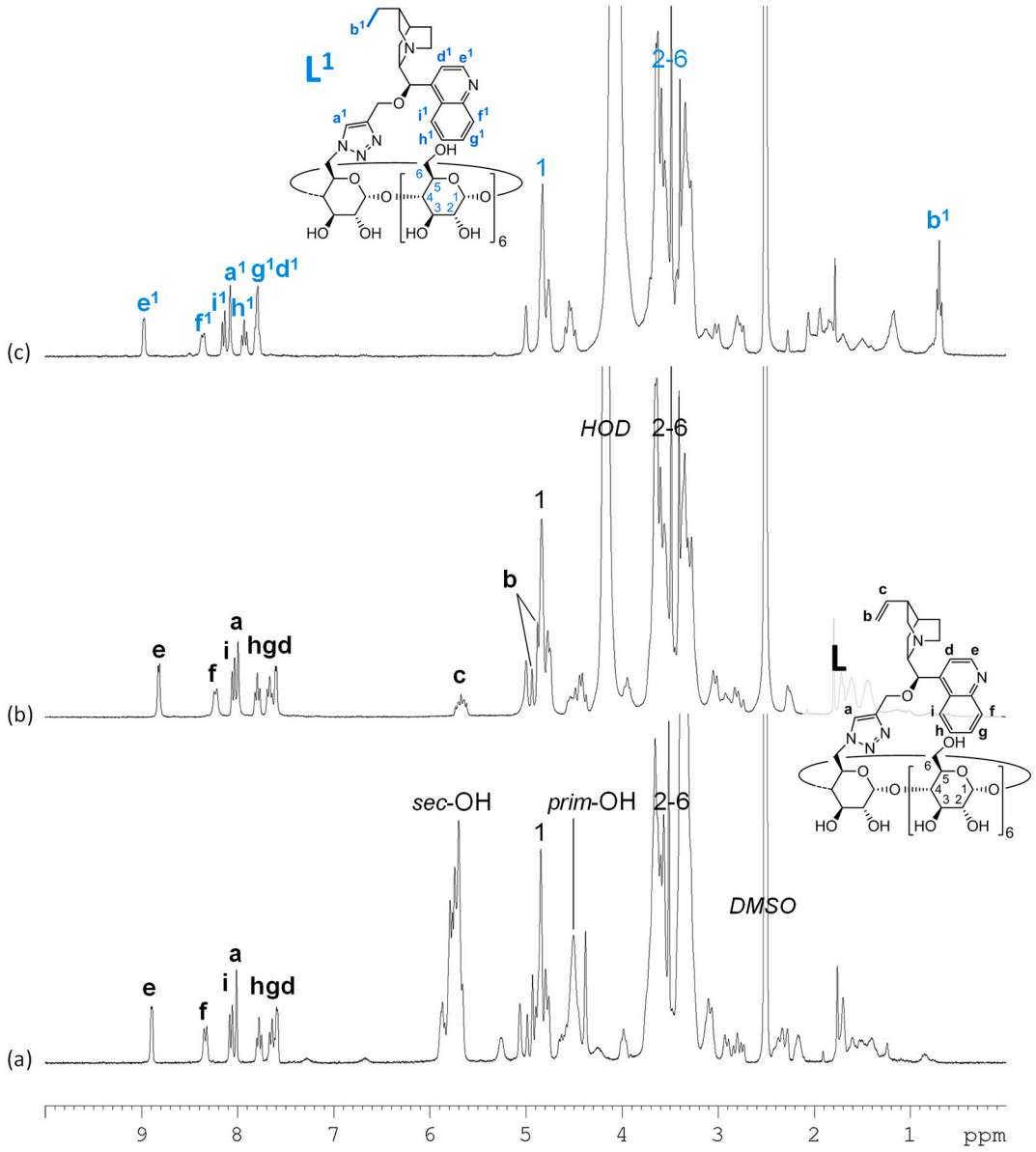


Fig. 2. ^{1}H NMR spectra of (a) **β**-CD-trz-Cin in DMSO-D_6, (b) **β**-CD-trz-Cin in DMSO-D_6/D_2O: 70/30, (c) **β**-CD-trz-Cin after 18 h at RT in water with H_2PtCl_6 and $NaBH_4$.
(DMSO-D_6/D_2O: 70/30).

previous studies, the use of 10 equivalents of stabilizing agent with respect to platinum did not allow the reduction of the platinum precursor (no color change of the solution during the reduction step and no Pt particles observed by TEM). This singular behaviour could be explained by the presence of the triazole group, which is known to interact strongly with the metal species [23]. Knowing that the solubility of β-CD-trz-Cin is very low (lower than 1 mg.mL^{-1}) and being sure that the cyclodextrin derivative is totally soluble [20], the best compromise was to work with a cyclodextrin/metal molar ratio of one, which was a sufficient but also a necessary amount to obtain Pt NPs. Several analyses were performed to characterize the platinum NPs in the liquid phase. First, we have checked by ^{1}H NMR if the cinchonidine-functionalized cyclodextrin structure (called **L**) was kept after the reduction step with sodium borohydride (Fig. 2).

The first ^{1}H NMR experiment (Fig. 2a) was performed in DMSO-D_6. The obtained signals were consistent with those previously described in the literature for **L** [20]. To get a precise assignment of the ethylenic methyne proton **c**, D_2O was added for the isotopic exchange of the cyclodextrin hydroxyl protons. This way, the NMR signal of the internal proton **c** of the vinyl group could also be clearly observed at 5.8 ppm (Fig. 2b). After the addition of $NaBH_4$, reduction of the platinum precursor has occurred but changes were observed both in the ethylenic protons (4.8–6 ppm) and in the aliphatic protons regions (0.5–2 ppm). The **c** proton signal has disappeared and a triplet at 0.8 ppm (**b^{1}**) has grown, proving the reduction of the vinyl group (Fig. 2c). The platinum NPs are finally not stabilized by β-CD-trz-Cin (named **L**), but by the reduced vinyl form (named **L^{1}**). The C═C double bond reduction during metal NPs synthesis by chemical reduction using sodium borohydride has already been observed [21]. The double bond reduction was confirmed by MALDI mass spectrometry as the signals of reduced β-CD-trz-Cin have been detected (see supporting information, Fig. S8).

The existence and the morphology of Pt NPs stabilized by **L^{1}** were then characterized by Transmission Electron Microscopy (Fig. 3).

According to the transmission electron micrograph at a magnification of × 200,000 and to the size distribution, we observed that platinum NPs were spherical and assembled in non-ordered structure with a mean

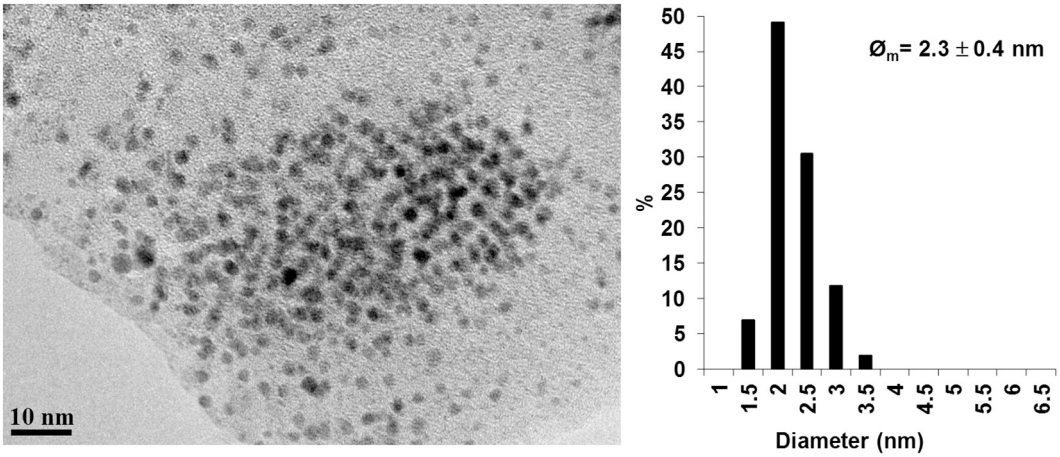
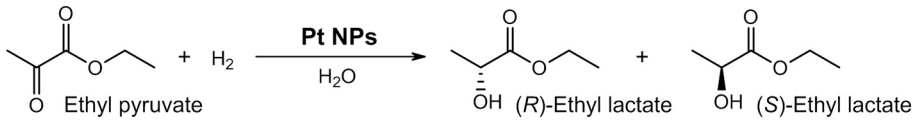


Fig. 3. Transmission electron micrograph at a magnification of × 200,000 and its corresponding size distribution of Pt_**L**^{1} NPs.

Table 1
Hydrogenation of ethyl pyruvate in the presence of Pt NPs[a].



Entry	Stabilizer	NPs stability		Conv. [%][b]	*ee* [%][b,c]
		before catalysis	*after catalysis*		
1	**L**^{1}	Yes	Yes	100	63(*R*)
2[d]	Cinchonidine (CN)	No	–	–	–
3[e]	β-CD-trz-CH$_2$OH + CN	No	–	–	–
4[f]	β-CD-trz-CH$_2$OH + CN	Yes	No	38	15(*R*)
5[e]	β-CD + CN	No	–	–	–
6[f]	β-CD + CN	No	–	–	–

[a] Reaction conditions: Pt (4 μmol), stabilizer (4 μmol), ethyl pyruvate (2 mmol), hydrogen pressure (40 bar), temperature (30 °C), stirring rate (1000 rpm), 6 mL water, reaction time (15 min). [b] conversion and enantiomeric excess were determined by GC analysis. [c] predominant configuration in brackets. [d] CN (4 μmol). [e] prepared by mixing cyclodextrin (4 μmol) and CN (4 μmol). [f] Pt NPs stabilized by cyclodextrin (4 μmol), followed by addition of CN (4 μmol), 24 h after the reducing step.

diameter of 2.3 nm ± 0.4 nm. This kind of dispersion has already been observed in previous studies concerning metal NPs stabilized by cyclodextrins [18].

The catalytic activity of the platinum colloidal suspension stabilized by **L**^{1} was evaluated in the aqueous biphasic hydrogenation of ethyl pyruvate (Table 1). Catalytic tests were performed at 30 °C under 40 bar of hydrogen with a substrate/metal molar ratio of 500. The reaction was monitored by gas chromatography analyses. For comparison, control experiments were also carried out considering the same reaction conditions.

The use of **L**^{1} (formed *in situ*, during the catalyst synthesis) appeared to be an efficient protective agent for the production of stable Pt colloidal suspension during the catalytic reaction (entry 1) and no trace of aggregation or aging of the particles was observed. The complete ethyl pyruvate conversion into ethyl lactate within 15 min was obtained with a good enantiomeric excess value of 63% towards the (*R*)-ethyl lactate. To show the positive effect of this stabilizing agent, we have first checked if cinchonidine alone was able to stabilize Pt NPs in aqueous medium (entry 2). Under our concentration conditions (one molar equivalent of cinchonidine with respect to platinum), a total metal sedimentation has occurred after the reducing step.

To show the beneficial effect of the covalent link between the cyclodextrin and cinchonidine, the Pt NPs synthesis was performed using a physical mixture corresponding to **L** (β-CD-trz-CH$_2$OH and cinchonidine) (entry 3). Unfortunately, the resulting colloidal suspension was unstable. As in the case of cinchonidine alone, total metal sedimentation was observed.

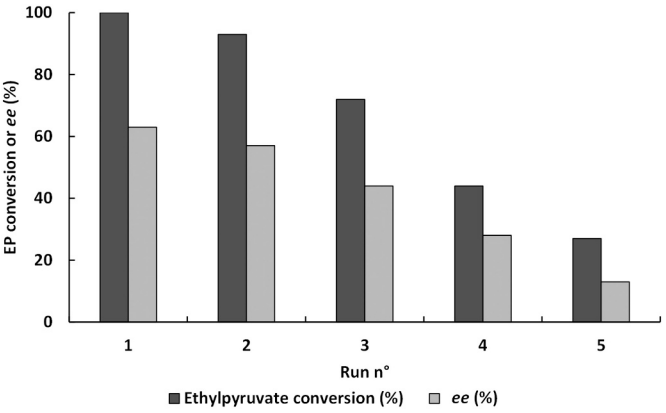


Fig. 4. Reusability of Pt_**L**^{1} in the hydrogenation of ethyl pyruvate. Reaction conditions: Pt (4 μmol), ethyl pyruvate (2 mmol), hydrogen pressure (40 bar), temperature (30 °C), stirring rate (1000 rpm), water (6 mL), reaction time (15 min).

We decided to change the synthesis procedure by first synthesizing Pt NPs stabilized with β-CD-trz-CH$_2$OH followed by the addition of cinchonidine, 24 h later (entry 4). However, this catalytic system was not stable during the hydrogenation reaction due to the platinum

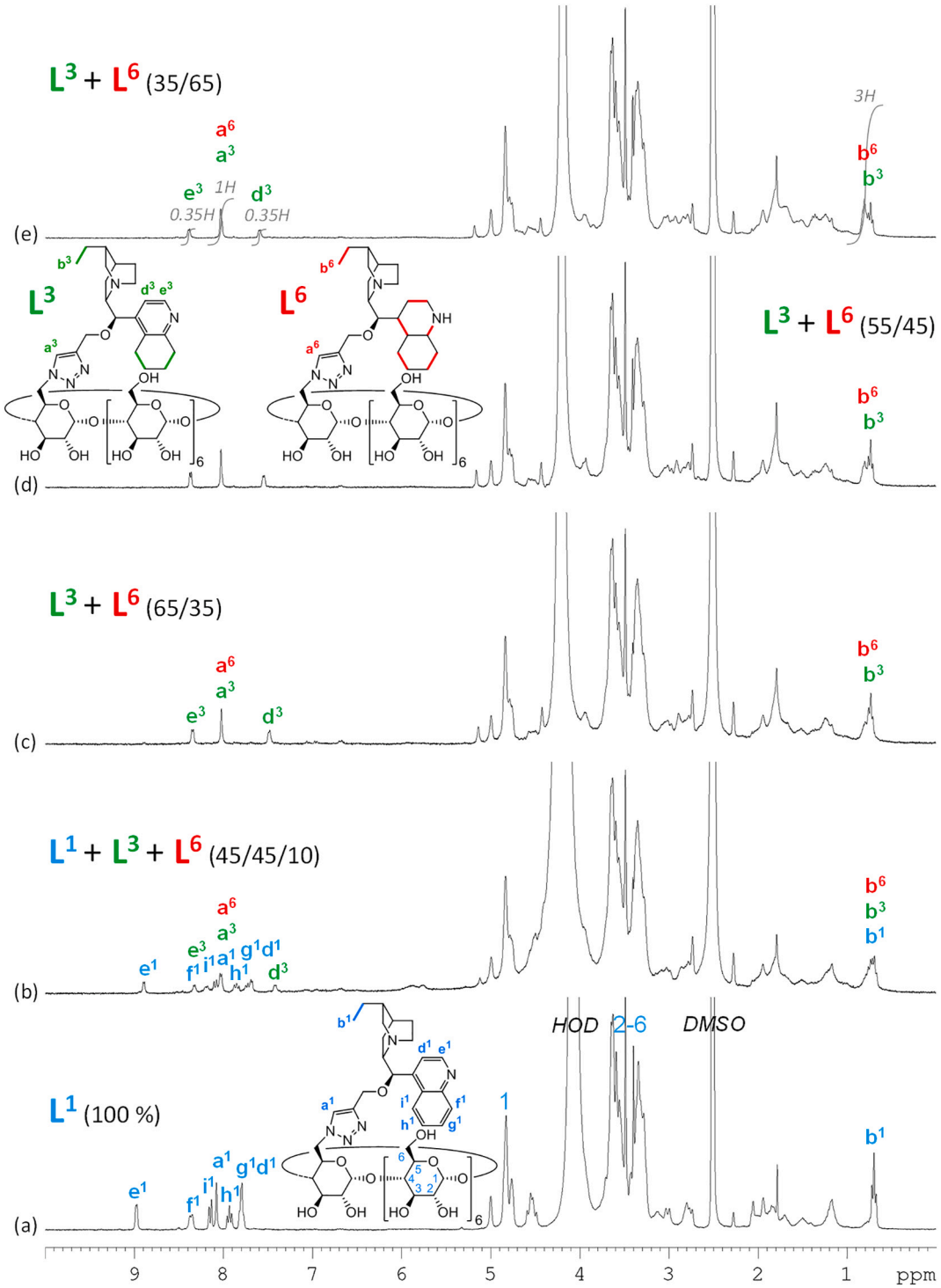


Fig. 5. ^{1}H NMR spectrum of (a) **β**-CD-trz-Cin after 18 h with H_2PtCl_6 and $NaBH_4$ at RT and then after (b) 15 min, (c) 30 min, (d) 60 min and (e) 120 min at 30 °C under 40 bar of H_2.
(DMSO-D_6/D_2O: 70/30; 300 MHz).

sedimentation in the bottom of the glass reactor. The enantiomeric excess did not exceed 15%. This enantiomeric excess was essentially due to the cinchonidine ring, *ee* with Pt NPs stabilized just by β-CD-trz-CH_2OH being negligible (< 5%). All these controls emphasized the beneficial effect of the cyclodextrin-functionalized cinchonidine in terms of stability, catalytic activity but also enantioselectivity. The same experiments were performed with β-CD but led to unstable colloidal suspensions during the preparation step (entries 5 and 6).

The results obtained with the Pt NPs stabilized by **L^1** were compared to those described in the literature with other cinchonidine-based Pt NPs, showing that the developed system gave relatively good values of activity and enantioselectivity in ethyl pyruvate hydrogenation (see supporting information, IV., Table S2).

The reusability of **L^1** stabilized Pt NPs was further investigated keeping ethyl pyruvate as substrate (Fig. 4), under the same catalytic conditions. After 15 min, products were extracted with chloroform and a

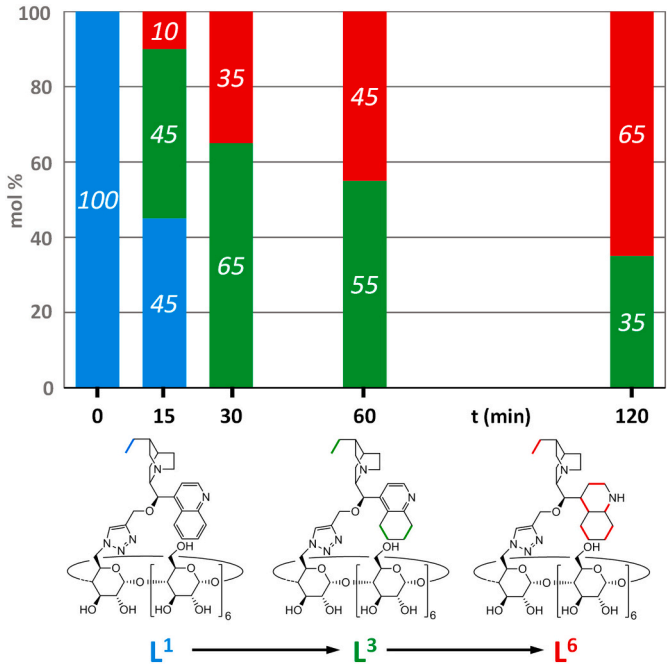


Fig. 6. Platinum catalyzed transformation of $\mathbf{L^1}$ into $\mathbf{L^3}$ and then $\mathbf{L^6}$ with time under 40 bar of hydrogen, at 30 °C.

second run could occur.

According to the experiments, catalytic activity and enantiomeric excess both decreased as runs progressed. Please note that a small metal sedimentation was observed after the third run, that means a NPs agglomeration in the aqueous layer involved in runs 3, 4 and 5. Leading to black platinum visible to the naked eye, this colloidal suspension instability was thought to be directly responsible of the observed catalytic activity decrease. A Pt NPs leaching, which could also occur during the extraction of ethyl lactate and residual ethyl pyruvate after each run, seems less probable. Indeed, stirring each organic layer obtained along the recycling experiments with added ethyl pyruvate (1 mmol) and in the reaction conditions (30 °C, 40 bar of H_2), showed no evolution in the sample composition even after 24 h. To understand what could be the origin of the instability of the aqueous colloidal suspension, which seemed to also undergo an enantioselectivity decrease along the recycling experiments, ^{1}H NMR of the aqueous phase was performed after the fifth run in order to check if the structure of the stabilizing agent $\mathbf{L^1}$ was kept. According to the ^{1}H NMR spectrum, the aromatic region (7–9 ppm) deeply changed (see supporting information, Fig. S4).

To rationalize this data, the platinum NPs stabilized by $\mathbf{L^1}$ were analyzed by ^{1}H NMR and MALDI spectroscopies, after being placed under catalytic conditions (40 bar of hydrogen, 30 °C) during different times (15, 30, 60 and 120 min) but without ethyl pyruvate. A blackening of the solution followed by a progressive metal sedimentation were observed with time. Moreover, NMR analyses (Fig. 5) and MALDI experiments (see supporting information, III.) proved that the quinoline moiety of $\mathbf{L^1}$ was hydrogenated with time in two steps: benzene ring hydrogenation and then pyridine ring hydrogenation.

These successive hydrogenations of the cyclodextrin graft leading to the transformation of $\mathbf{L^1}$ to $\mathbf{L^3}$ and then to $\mathbf{L^6}$ can be quantified by the NMR spectra integrations (see supporting information, II.5) showing for example that, after 1 h under 40 bar of H_2 and without ethyl pyruvate, $\mathbf{L^1}$ has led to 55% of $\mathbf{L^3}$ and 45% of $\mathbf{L^6}$ (Fig. 6).

The same yields of 55% and 45% for $\mathbf{L^3}$ and $\mathbf{L^6}$ were estimated after five runs of Pt_$\mathbf{L^1}$ NPs catalyzed ethyl pyruvate hydrogenation, showing that the cyclodextrin graft hydrogenation was a little bit slower in the presence of the ethyl pyruvate substrate as a competitor (see supporting information, Fig. S5). Nevertheless, this denaturation of the chiral inductor graft is probably responsible for the less efficient both stabilizing and enantioselective properties observed with time. Contrary to the quinoline part, the triazole ring was perfectly stable in these hydrogenation conditions. This result is consistent with a perfect integrity of β-CD-trz-CH_2OH under hydrogen at 30 °C (see supporting information, Fig. S7).

4. Conclusion

In this paper, we showed that a cinchonidine-functionalized β-cyclodextrin synthesized by crosslinking mono azido-β-CD with *O*-propargyl cinchonidine was a good candidate for the synthesis of catalytically active platinum nanoparticles for the asymmetric hydrogenation of ethyl pyruvate in water. The chemical reduction of Pt (IV) species by sodium borohydride provided stable Pt colloidal suspensions organized into non-ordered superstructures with narrow size distributions. Control experiments have clearly shown the beneficial effect of the covalently linkage between cyclodextrin and cinchonidine. The platinum NPs were catalytically active towards ethyl pyruvate hydrogenation, with 63% of enantiomeric excess. Nevertheless, the recovery and the recycling of the platinum NPs were difficult to realize, due to the instability of the stabilizing agent in presence of Pt NPs under high hydrogen pressure. Other metals are under investigation to avoid the aromatic reduction.

Declaration of Competing Interest

None.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2020.106272.

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