Chiral Imprinting of Palladium with Cinchona Alkaloids

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Materials and methods. A French Press was used for preparing the coins, applying a pressure of 10 tons/cm². All UV–visible experiments were done on a Varian Cary 50 Bio UV–visible Spectrophotometer. SEM was carried out on a Sirion (FEI) HRSEM instrument (operating voltage was 5kV). Powder XRD measurements were carried out on a Philips automated powder diffractometer (with PW3830 generator, 40 Kv, 40 mA and Cu Kα). N₂-BET surface areas and porosities were determined from nitrogen adsorption–desorption isotherms obtained with a Sorptomatic-1900 physisorption instrument. The photoelectron emission experiments were performed done using a ArF excimer laser which produces 193 nm photons corresponding to energy of 6.42 eV with a
pulse width of ~20 nsec. GC analysis for determining enantiomeric excess was performed on an Interscience GC-8000 gas chromatograph with a fused silica chiral capillary column (DBEXm, permethylated β-cyclodextrin doped into 14% cyanopropylphenyl/86% dimethyl polysiloxane, 30 m × 0.25 mm × 0.25 mm). GC conditions: isotherm at 90 ºC (25 min); ramp at 25 ºC min⁻¹ to 220 ºC; isotherm at 220 ºC (7 min). Pentadecane was used as internal standard. Unless otherwise noted, all chemicals were purchased from commercial sources and used as received. Demineralized water was used in all experiments.

Control experiments

**Stability of the dopants to the reaction conditions.** All dopants were checked for their stability towards the reducing agent hypophosphite and found to be stable. Typically, 0.01 g of alkaloid was poured into a stirred solution of SDS (0.9 g) in 175 ml of water. 1.2 g of NaH₂PO₂ was added and the resulting solution was stirred for 2 h at 25 ºC. Spectra before and after the exposure to the reducing agent were compared, and found, to be identical.

**Adsorption vs entrapment experiments.** For comparing entrapment to adsorption, the following experiments were carried out: The Pd matrix was prepared as described before but without an entrapped molecule. Then 0.001 g of CN and 0.1 g of Pd were stirred in 20 ml SDS/H₂O during 24 hours. The amount adsorbed was determined spectroscopically from the supernatant solution. We found that only 15% of CN was adsorbed over Pd vs. 100% when the entrapment is performed.
**Extraction experiments.** Extraction of the entrapped molecules into different solvents was tested by stirring 0.1 g of the doped metal with 20 ml of water, SDS/H₂O, THF and DMSO. The amount of each alkaloid before and after the extraction were compared and quantified by GC analysis. No extraction was observed for either water or SDS/H₂O. Complete extraction (>99%) was achieved both with THF or DMSO. The amount of remaining alkaloid inside the pores after extraction was ≤0.01% relative to Pd.

**In situ Uv–visible re-adsorption experiments**

In a quartz cuvette, 0.01 g of CN@Pd was added to a solution of 0.1 mg of CN or CD in 1 ml SDS/H₂O. The samples were stirred for 15 h and *in situ* UV–visible spectra of the supernatant solution were recorded. For the experiments with the “alkaloid-free” palladium the same protocol was followed. See Figure S1.

**Enantioselective photoelectron emission experiments**

The samples were inserted into an ultrahigh vacuum chamber at >108 mbar. The photoelectrons were ejected from the substrate by applying a laser beam at 193 nm (6.4 eV) using λ/4 plate to create either *cw* or *ccw* circularly polarized light. The ejected electron energy distribution is analyzed by using a time-off-spectrometer. The laser energy is maintained very low (20 pJ per pulse) to avoid any nonlinear processes. Pure Pd, prepared in the absence or presence of SDS, were measured as blank experiments (Figure S2).
**Figure S2.** The electron energy distribution profiles obtained for photoelectrons ejected by either *cw*-CPL or *ccw*-CPL from: (A) pure pre-prepared Pd, (B) pure pre-prepared Pd with SDS. It is seen that the *cw* and *ccw* curves coincide (top overlapping two curves). For comparison, this figure shows also the energy distribution obtained with linear (i.e., non-polarized) light.
**Figure S1.** Adsorption spectra of $CN$ (A) and $CD$ (B) in extracted $CN@Pd$; and $CN$ (C) and $CD$ (D) in pre-prepared Pd without dopant.
Enantioselective hydrogenation catalysis experiments.

Procedure for the transfer hydrogenation of acetophenone to phenylethanol. The reaction vessel, under nitrogen atmosphere, was filled with isopropanol (20 ml), acetophenone (0.058 ml, 0.50 mmol), CN@Pd catalyst (0.005 g, 1 mol %) and potassium isopropanate (5 % w/v solution in isopropanol, 0.025 ml, 12.5 μmol). The resulting mixture was stirred for 8 h at 25 °C and the reaction progress was monitored by GC.

Procedure for the hydrogenation of isophorone to dihydroisophorone. The reaction vessel was filled with isophorone (1.0 mmol, 150 μl), CN@Pd catalyst (0.05 g, 10 mol %) and EtOH (20 ml). Then the vessel was filled with hydrogen (60 mmHg) and stirred for 10 h at 25 °C. The reaction progress was monitored by GC. The reaction were performed as above when CD@Pd, QN@Pd or QD@ Pd were used as catalysts.