Electronic Supporting Information

Ferrocenyl-terminated polyphenylene-type dendrimers as supports for gold and palladium nanocatalysis

Wenjuan Wang,[a,b] Elena S. Serkova[c], Eduardo Guisasola Cal,[d] Desire Di Silvio,[e] Marta Martínez Moro,[d] Sergio Moya,[d] Jean-René Hamon,[b] Didier Astruc[a,]* and Zinaida B. Shifrina[c,]*

a. *ISM, UMR CNRS 5255, Université de Bordeaux, Talence 33405 Cedex, France. E-mail: didier.astruc@u-bordeaux.fr*

b. *Institut des Sciences Chimiques, UMR CNRS 6226, Université de Rennes 1, 35042 Rennes Cedex, France.*

c. *A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Moscow 119991, Russia. E-mail: z_shifrina@yahoo.com*

d. *Soft Matter Nanotechnology Lab, CIC biomaGUNE, Paseo Miramón 182, 20014 Donostia-San Sebastián, Gipuzkoa, Spain.*

e. *Surface Analysis and Fabrication Platform Manager, Parque Científico y Tecnológico de Gipuzkoa, Paseo Miramón 194, 20014 Donostia / San Sebastián · Gipuzkoa · Spain.*

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1. General data

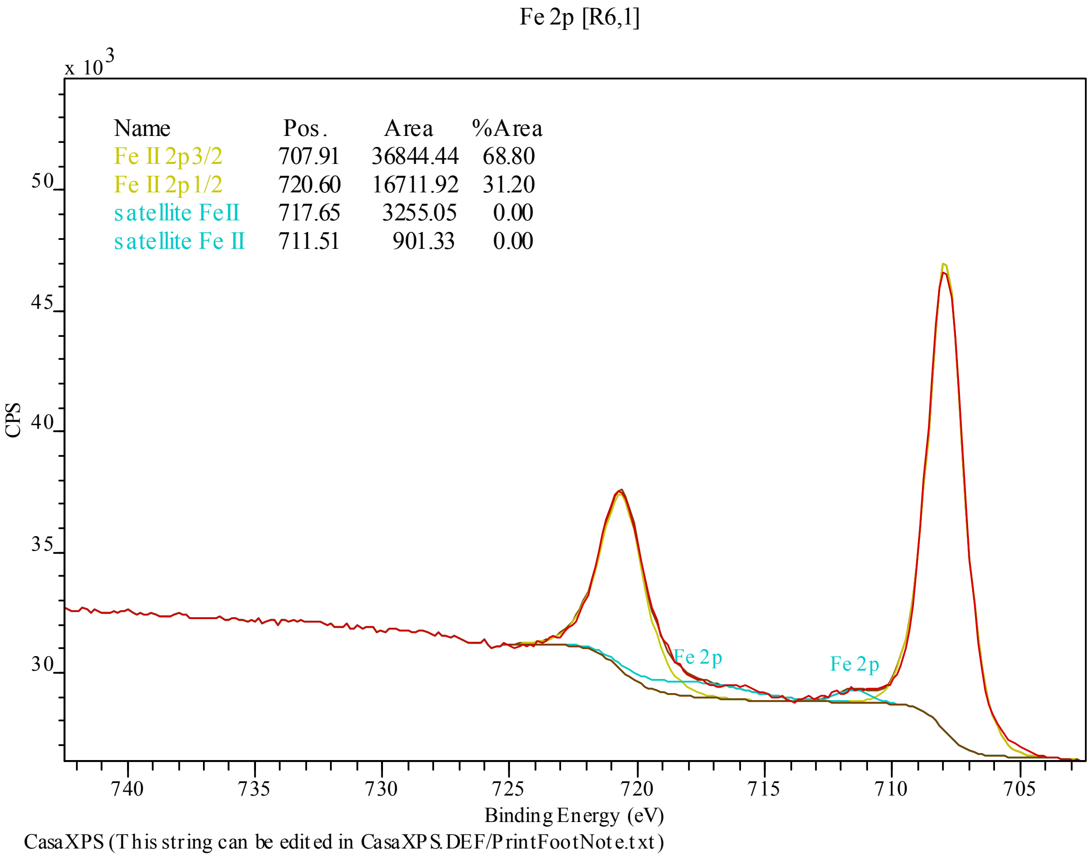
All the solvents and chemicals were used as received. ^{1}H NMR spectra were recorded at 25 °C with a Bruker AC 300 MHz. All the chemical shifts are reported in parts per million (δ, ppm) with reference to Me_4Si in $CDCl_3$. Transmission Electron Microscopy (TEM): The sizes of the MNPs were determined by TEM using a JEOL JEM 1400 (120 kV) microscope. The TEM samples were prepared by deposition of the nanoparticle suspension (10 µL) onto a carbon-coated microscopy copper grid. X-ray Photoelectron Spectroscopy (XPS): System: SPECS SAGE HR; X-Ray source: Al Kα non-monochromatic; operated at 12.5 kV and 300 W. Take off angle 90^o, at ~10^{-8} Torr. Pass energy for survey spectra 30 eV, 10 eV for narrow scans analysis; spectra are calibrated to C-C carbon 285 eV. Analysis is consisted of Shirley background subtraction. Peaks are fitted with symmetrical Gaussian-Lorentizan (GL) line shapes. Samples are prepared by dehydration on the titania coated glass or silica substrates. Titania is selected as a substrate to avoid the overlap of Si and Au. Flash column chromatography was performed using silica gel (300-400 mesh).

2. The XPS data of Fe 2p in FcMTD alone, Pd(II)-FcMTPD and Pd(0) NP@FcMTPD.

Table S1 The XPS data of Fe 2p in FcMTD alone, Pd(II)-FcMTPD and Pd(0) NP@FcMTPD.

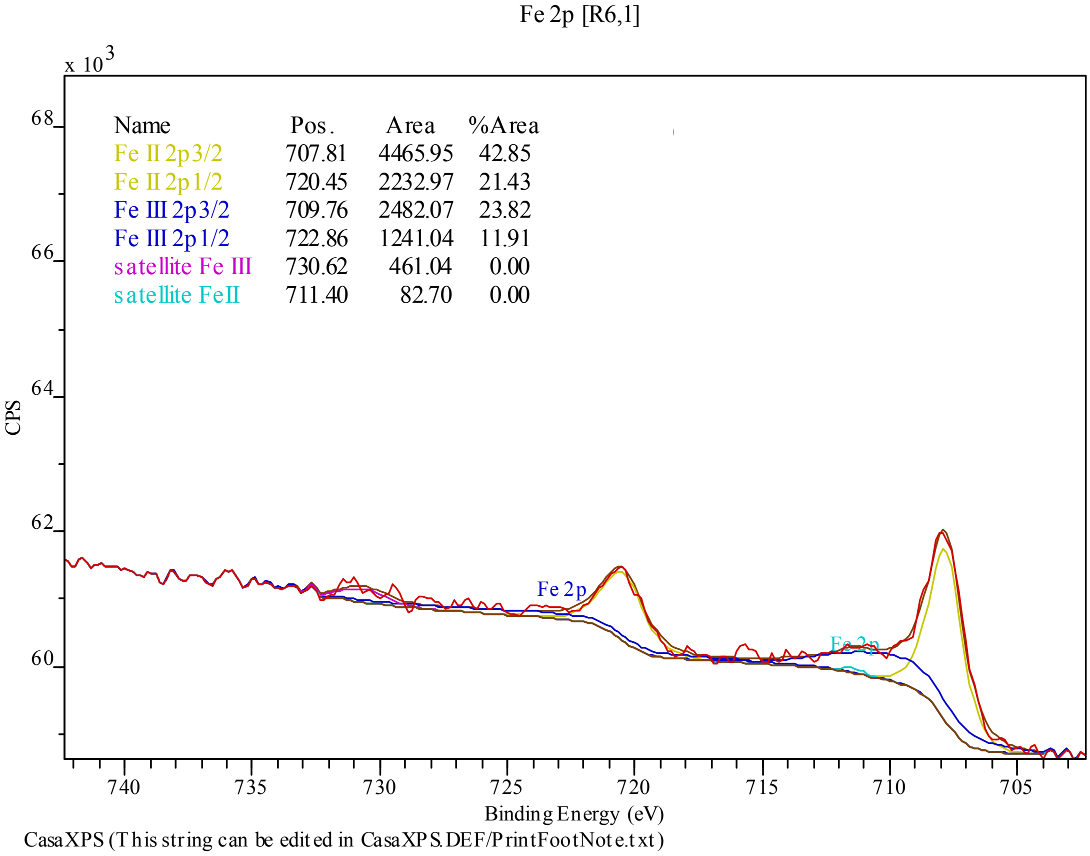
	Fe II 2p3/2 BE(eV) [at%]	**Fe III 2p3/2 BE(eV) [at%]**
FcMTD	707.9 [100]	-
FcMTD + Pd^{2+}	707.8 [64]	709.8 [36]
FcMTD -PdNPs	707.7 [100]	**-**

Fe 2p in **FcMTD** sample showed the typical spectrum for ferrocene with two satellites. In **FcMTD + Pd^{2+}** three peaks appeared (2p 3/2 709.8 eV, 2p ½ 722.9 eV, satellite 730.6 eV) that are compatible with Fe(III).[4,5] Fe 2p in **FcMTD -PdNPs** sample showed the typical spectrum for ferrocene, but the high S/N does not allow to appreciate the two satellites at about 711eV and 718 eV.



Name	Pos.	Area	%Area
Fe II 2p3/2	707.91	36844.44	68.80
Fe II 2p1/2	720.60	16711.92	31.20
satellite FeII	717.65	3255.05	0.00
satellite Fe II	711.51	901.33	0.00

Fig. S1. XPS spectra of Fe 2p in the sample FcMTD alone.



Name	Pos.	Area	%Area
Fe II 2p3/2	707.81	4465.95	42.85
Fe II 2p1/2	720.45	2232.97	21.43
Fe III 2p3/2	709.76	2482.07	23.82
Fe III 2p1/2	722.86	1241.04	11.91
satellite Fe III	730.62	461.04	0.00
satellite FeII	711.40	82.70	0.00

Fig. S2. XPS spectra of Fe 2p in the sample Pd(II)-FcMTPD.

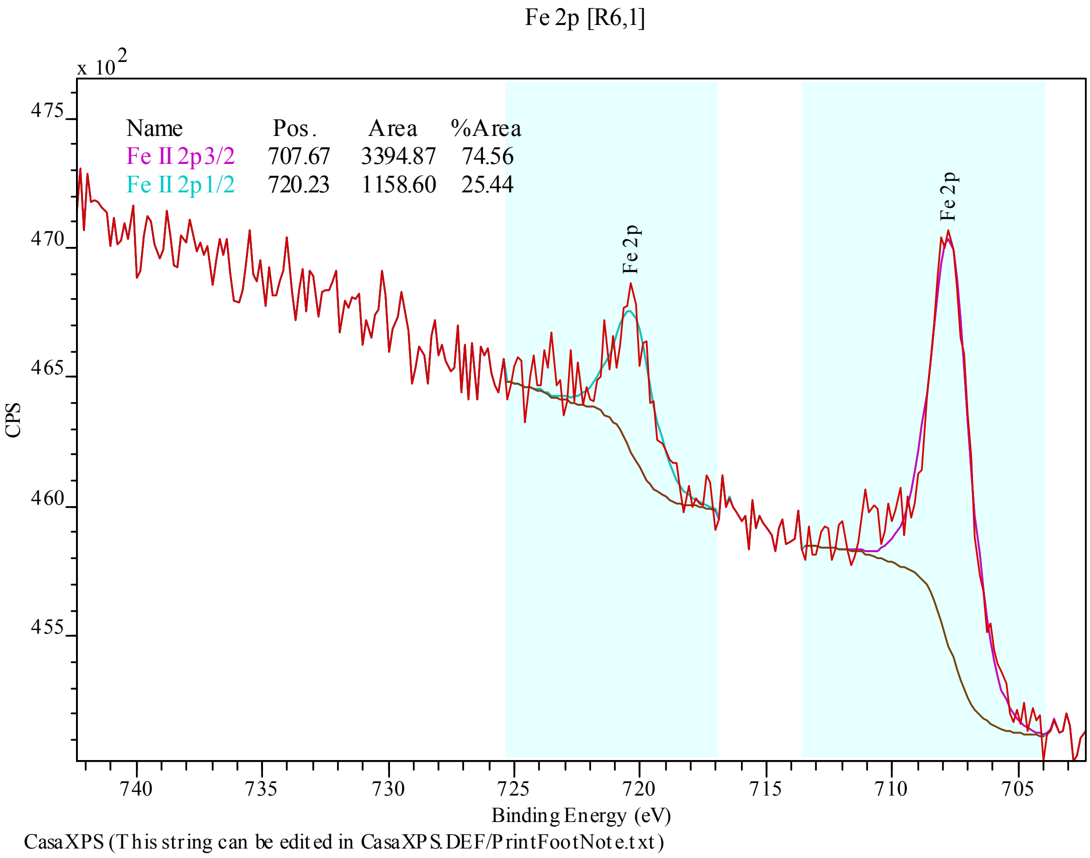


Fig. S3. XPS spectra of Fe 2p in the sample Pd(0) NP@FcMTPD.

3. UV-vis. spectrum of FcMTD-stabilized PdNPs-1 and PdNPs-2

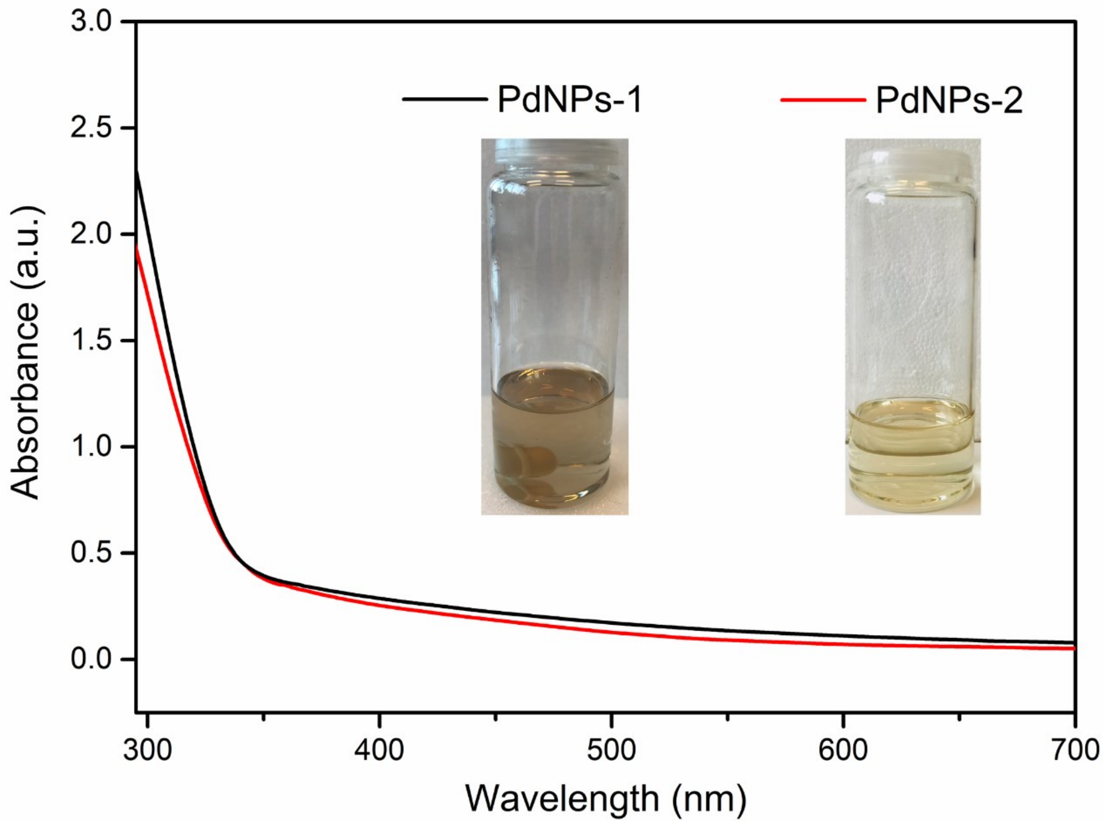


Fig. S4 UV-vis. spectrum of FcMTD -stabilized PdNPs-1 and PdNPs-2. Insert: the photograph of PdNPs-1 (left) and PdNPs-2 (right).

4. Determination of the rate constant k_{app} of the 4-nitrophenol reduction reaction

The reaction is fitted with a pseudo-first-order kinetics with respect to 4-NP in the presence of excess $NaBH_4$, leading to the determination of the rate constant k_{app} (eqn (1)):

$$-\ln(C_t/C_0) = k_{\mathrm{app}}t \quad (1)$$

(C_t is the concentration of 4-NP at a time t, and C_0 is the concentration of 4-NP at time t = 0).

5. Synthesis of the MNPs-3 stabilized by FcMTPD.

FcMTPD was prepared according to the literature procedure by copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction between a previously reported ethynyl-terminated dendrimer and azidomethylferrocene. Then, a solution (V_{CH2Cl2}/ V_{MeOH} = 30:1, 6.8 mL) of Na_2PdCl_4 (or $HAuCl_4$, 1.0×10^{-3} mmol, n_{metal}: n ($_{Triazole + Pyridine}$) = 1:1) was mixed with a solution (V_{CH2Cl2}/ $V_{methanol}$ = 30:1, 3 mL) of the dendrimer FcMTPD (2.5×10^{-5} mmol) in a 20 mL flask with a stir bar. After the mixture was stirred for 30 min, then 5.0×10^{-3} mmol of $NaBH_4$ was added into the flask under vigorous stirring. After continuous stirring for 1 h at room temperature, the metal nanoparticles were obtained.

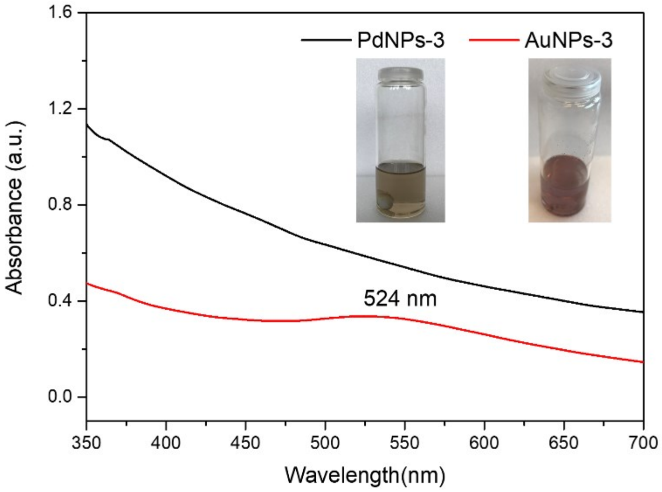


Fig. S5 UV-vis. spectrum of FcMTD-stabilized PdNPs-3 and AuNPs-3. Insert: the photograph of PdNPs-3 (left) and AuNPs-3 (right).

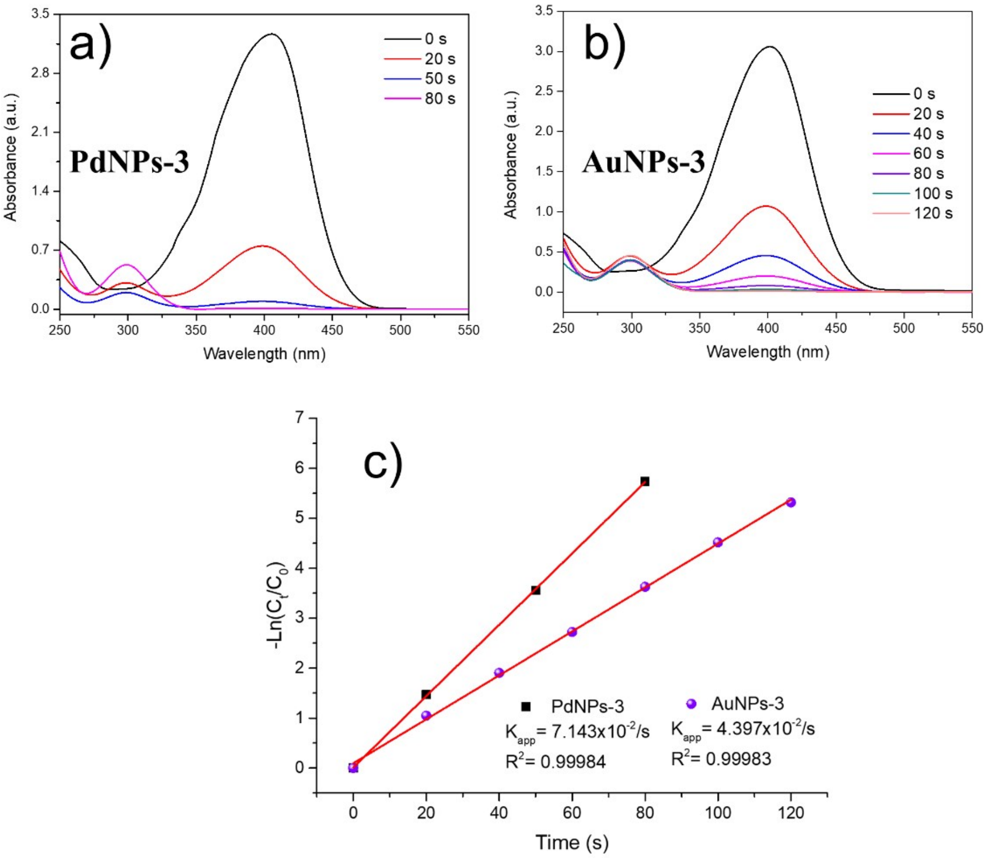


Fig. S6. Time-dependent UV-vis. spectrum of the *p*-nitrophenol reduction reaction in the presence of 0.5% mmol of PdNPs-3 (a) and AuNPs-3 (b). (c) Plots of the consumption rate of 4-NP: [-ln (C_t/C_0)] *vs.* reaction time with 0.5% mmol of MNPs-3.

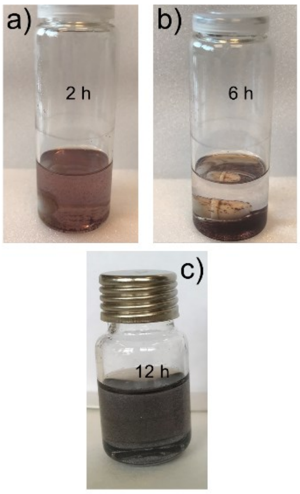


Fig. S7. The photograph of AuNPs-3 (a, b) and PdNPs-3 (c).

6. TEM images and size distribution histogram of MNPs-1 and their UV-vis. spectrum after the 1st cycle

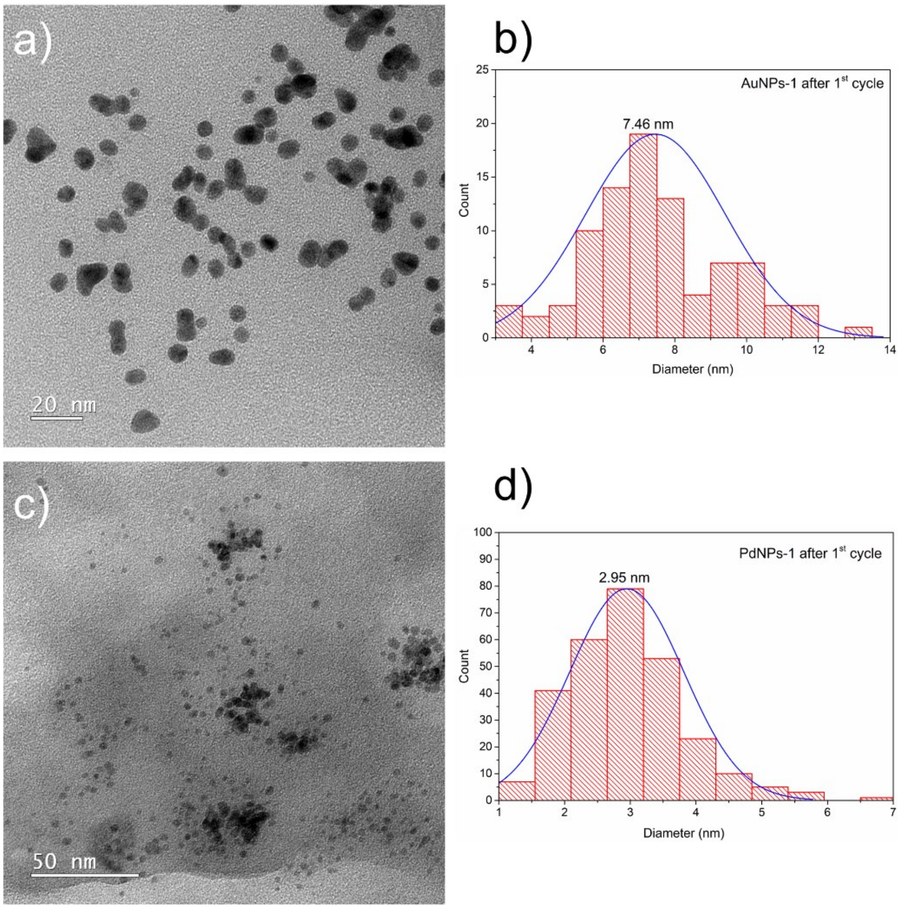


Fig. S8. TEM images of PdNPs-1 (a) and AuNPs-1 (c) after the 1st cycle; size distribution histogram of PdNPs-1 (b) and AuNPs-1 (d) after 1st the cycle.

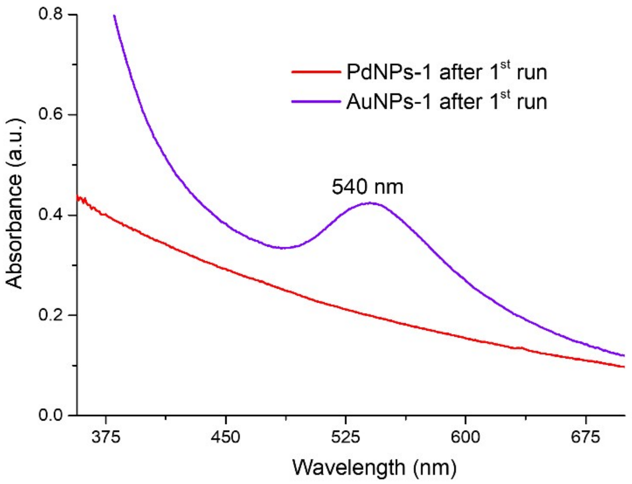


Fig. S9 UV-vis. spectrum of FcMTD-stabilized PdNPs-1 and AuNPs-1 after 1st run.

7. Calculation of the NP surface atoms number (Ns) and k_0 related to the Ns.

$V_{NP} = NV_{atom}$ (eq. 1)

$4/3\pi(R_{NP})^3 = N\ 4/3\pi(R_{atom})^3$ (eq. 2)

Where V is the atom volume of the NP, R is the atomic radius of the NP, and N is the total number of atoms within the NP. Rearranging, we obtain:

$N = (R_{NP}/R_{atom})^3$ (eq. 3)

Knowing the NP radius, we can also calculate the surface area of a NP with the following equation:

$S_{NP} = 4\pi(R_{NP})^2$ (eq. 4)

$N'_{NP} = (N_M/N) \times 6.02\times10^{23}$ (eq. 5)

$S = S_{NP}\ N'_{NP}$ (eq. 6)

Normalized to the unit volume of the system, where N'_{NP} is the total number of metal nanoparticles, S is total surface area of metal nanoparticles, N_M is the molar of metal nanoparticles.

$k_{app} = k_0\ S$ (eq. 7)[1]

Table S2. Physical properties and catalytic efficiencies of the nanocatalysts.

	R_{atom} [a] (nm)	R_{NP} [b] (nm)	k_{app} [c] (10^{-2} s^{-1})	k_0 [d, e] [$s^{-1}m^{-2}L$]	[N_M] [mmol/L]	S [d, f] [m^2/L]
PdNPs-1	0.137	1.0	7.80	0.348	1.15×10^{-2}	0.224
AuNPs-1	0.144	1.8	5.59	0.386		0.145
PdNPs-2	0.137	1.85	3.95	0.326		0.12
AuNPs-2	0.144	3.25	0.95	0.119		0.08

[a] Radius of the metal atomic. [b] Radius of the metal particles. [c] Apparent rate constant. [d] Calculated from the data given in the respective papers. [e] Rate constant normalized to the surface of the particles in the system (eq 7). [f] Surface area of metal nanoparticles normalized to the unit volume of the system.

Reference

1. Y. Mei, G. Sharma, Y. Lu and M. Ballauff, *Langmuir*, 2005, **21**, 12229-12234.