

ESI:

Bi/Trinuclear Pt_{1&2}Cu Clusters Assembly from Isolated Metal Atoms

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1. Experimental

1.1 Chemicals

Silica, Chloroplatinic acid, ethanol, CuCl_2 were purchased from Sinopharm Group Co., Ltd.. 1-octene was purchased from Aladdin. PDMS-PEG was purchased from Guangzhou Tinci Materials Technology Co., Ltd. The molecular weight of each block is 30,000 for PDMS and 545 for PEG-12. Ultrapure water purified by Milli-Q Advantage A10 was used.

1.2 Samples preparation

Preparation of $\text{Pt}_1@$ PDMS-PEG stock solution by reduction of H_2PtCl_6 with ethanol: PDMS-PEG (0.6465 g), ethanol (135 ml), and ultrapure water (10.2 ml) were stirred in a round bottom flask at 450 rpm at RT. After 10 minutes 4.8 ml H_2PtCl_6 solution (1.84×10^{-2} mol/L) was added, and the mixture was stirred for 10 more minutes. The solution was refluxed at 105 °C for 3 h and then cooled to RT. (For NMR characterization, ethanol and water were evaporated at 40 °C under reduced pressure)

Preparation of $\text{CuCl}_2@$ PDMS-PEG stock solution: PDMS-PEG (0.6465 g), ethanol (135 ml), and ultrapure water (10.2 ml) were stirred in a round bottom flask at 450 rpm at RT. After 10 minutes 4.8 ml CuCl_2 solution (1.84×10^{-2} mol/L) was added, and the mixture was stirred.

Preparation of $\text{PtCu}@$ PDMS-PEG stock solution by reduction of CuCl_2 with ethanol: $\text{Pt}_1@$ PDMS-PEG stock solution (150 ml), was placed in a round bottom flask at RT. A 4.8 ml CuCl_2 solution (1.84×10^{-2} mol/L) was added and the mixture was stirred. Purge N_2 into the flask to remove air for 30 more minutes. The solution was refluxed

at 80 °C for 7 h and then cooled to RT. (For NMR characterization, ethanol and water were evaporated at 40 °C under reduced pressure)

Preparation of CuCl₂_Pt@PDMS-PEG stock solution: Pt₁@PDMS-PEG stock solution (150 ml), was placed in a round bottom flask and. 4.8 ml CuCl₂ solution (1.84×10^{-2} mol/L) was added and the mixture was stirred at 450 rpm at RT.

Preparation of Pt₁@PDMS-PEG/SiO₂: A calculated amount of silica based on the desired final Pt loading was added to 150 ml Pt₁@PDMS-PEG stock solution and stirred for 1 h. Ethanol and water were removed at 40 °C under vacuum. The sample was further vacuum dried for 12 h at 40 °C.

Preparation of CuCl₂@PDMS-PEG/SiO₂: A calculated amount of silica based on the desired final Pt loading was added to 150 ml CuCl₂@PDMS-PEG stock solution and stirred for 1 h. Ethanol and water were removed at 40 °C under vacuum. The sample was further vacuum dried for 12 h at 40 °C.

Preparation of PtCu@PDMS-PEG/SiO₂: A calculated amount of silica based on the desired final Pt loading was added to 150 ml PtCu@PDMS-PEG stock solution and stirred for 1 h. Ethanol and water were removed at 40 °C under vacuum. The sample was further vacuum dried for 12 h at 40 °C.

Preparation of CuCl₂_Pt@PDMS-PEG/SiO₂: A calculated amount of silica based on the desired final Pt loading was added to 150 ml CuCl₂_Pt @PDMS-PEG stock solution and stirred for 1 h. Ethanol and water were removed at 40 °C under vacuum. The sample was further vacuum dried for 12 h at 40 °C.

1.3 Characterization Details

Ultraviolet–visible (UV–Vis) spectra were collected on a Shimadzu UV-2600 spectrophotometer.

The surface composition and the binding energy (B.E.) of the catalysts were determined by X-ray photoelectron spectra (XPS) on an ESCALAB250 X-ray photoelectron spectrometer with SiO₂ as the internal standard (Si 2p = 103.4 eV).

The surface atomic ratio of Pt to Cu on the heteronuclear catalyst PtCu@PDMS-PEG/SiO₂ was calculated as the following equations.

$$\frac{n_i}{n_j} = \frac{I_i}{I_j} \times \frac{\sigma_j}{\sigma_i} \times \frac{E_{k_j}^{0.6}}{E_{k_i}^{0.6}}$$

$E_k = h\nu - E_b$; n: Number of atoms; I: Intensity; E_k : Kinetic energy; E_b : Binding energy photoionization cross section;

All solid-state NMR measurements were carried out on a 11.7 T wide-bore Bruker Avance III solid-state NMR spectrometer, operating at a Larmor frequency of 500.13 MHz for ¹H, 125.77 MHz for ¹³C, and 107.21 MHz for ¹⁹⁵Pt. A 4.0 mm Bruker multinuclear HX double resonance magic angle spinning (MAS) probe was used. The experiments were acquired at 25 °C and an MAS frequency of 10 kHz, controlled to within +/-3 Hz using the Bruker MAS controller. The typical 90° pulse length was 2.5 us (¹H), 3.6 us (¹³C), and 4.2 us (¹⁹⁵Pt). 76,200 scans were collected for ¹⁹⁵Pt MAS NMR spectra with a recycle delay of 1 s and 30° pulse excitation (1.4 us). 8,192 scans were collected for ¹³C MAS NMR spectra with a recycle delay of 3 s, where ¹H SPINAL-64 heteronuclear decoupling with field strength of 90 kHz was applied during the acquisition period. Solution NMR spectra were obtained on a Bruker

Avance III 600 MHz and a 400 MHz spectrometers using the 5 mm multinuclear probe. Single pulse and proton decoupling were used for ^{195}Pt and ^{13}C measurements with 3-second relaxation delay, respectively. The solution and solid-state ^{195}Pt NMR spectra were referenced to a platinum peak of a 1.2 M Na_2PtCl_6 D_2O solution. The chemical shifts of ^1H and ^{29}Si NMR spectra were referenced externally to TMS.

A Diffus IR diffuse reflectance accessory was used for the FTIR measurements. The accessory was purchased from Pike Technologies. The MIR instrument model is Thermo Scientific Nicolet iS50 with mercury cadmium telluride (MCT) detector. The resolution is 4 cm^{-1} for the DRIFT and measurements using 64 scans. The sample was evacuated at $25\text{ }^\circ\text{C}$ for 1h before the absorption of the high purity probing gas NO.

MALDI-TOF MS spectra were generated using an ABI MALDI TOF/TOF 5800 instrument. One μl of the solution was deposited directly on an MTP BigAnchorChip 384 TF target plate (Bruker Daltonics). The preparation was overlaid with $1\ \mu\text{l}$ of CHCA matrix solution, which was a saturated solution of alpha-cyano-4-hydroxycinnamic acid in 50% acetonitrile-2.5% trifluoroacetic acid. It was then air dried at room temperature to enable co-crystallization of CHCA with the experimental samples for MALDI TOF detection.

1.4 Hydrosilylation of 1-octene

The procedure for hydrosilylation of 1-octene with 1, 1, 3, 5, 5, 5-heptamethyltrisiloxane $((\text{Me}_3\text{SiO})_2\text{MeSiH})$ by Pt@PDMS-PEG and PtCu@PDMS-PEG was carried out as in the following. 0.034 ml catalyst stock solution (with Pt concentration at $1.16 \times 10^{-4}\text{ mol/L}$) was added into the reactor. Ethanol and water

were evacuated at RT. The reactor containing catalyst was then transferred into a glovebox. 4 mmol 1-octene was added and mixed with the catalyst [corresponding to $n(1\text{-octene}):n(\text{Pt})=1,000,000:1$] for 5 min at 25 °C before starting the reaction. 4.4 mmol $\text{Me}_3\text{SiO}_2\text{MeSiH}$ was then added, and the reaction was carried out at 70 °C. After reaction, 2 mmol *N,N*-dimethylaniline (0.2424 g) was added as an internal standard. Products and reactants were characterized by ^1H NMR (400 MHz, CDCl_3).

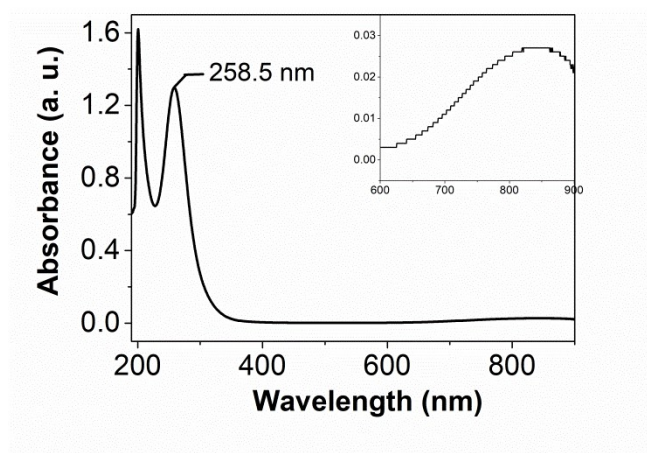


Fig. S1 The characteristic UV-Vis absorption peak of CuCl_2 at 258 nm and around 800 nm in PDMS-PEG/ethanol-water

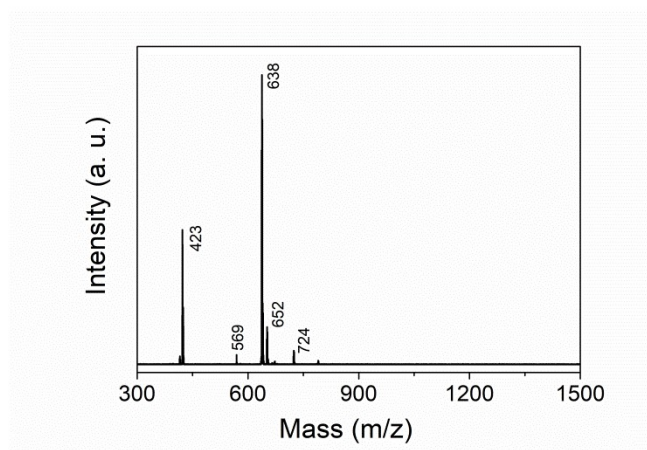


Fig. S2 MALDI-TOF spectrum of PtCu/PDMS-PEG/ethanol-water solution in the presence of phenanthroline

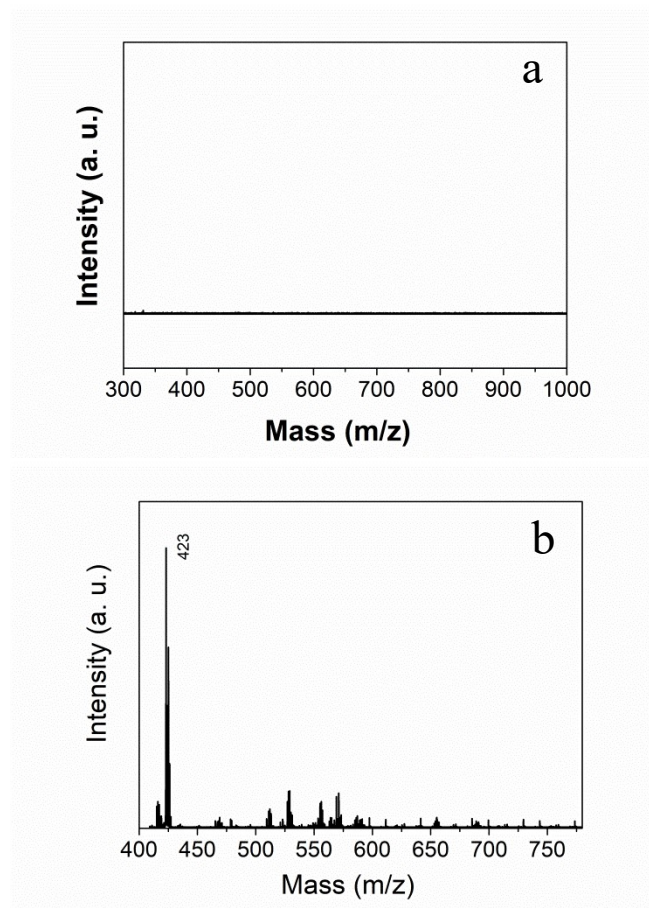


Fig. S3 (a) MALDI-TOF spectrum of PtCu@PDMS-PEG/ethanol-water solution in the absence of phenanthroline; (b) MALDI-TOF spectrum of CuCl₂_Pt@PDMS-PEG/ethanol-water solution in the presence of phenanthroline

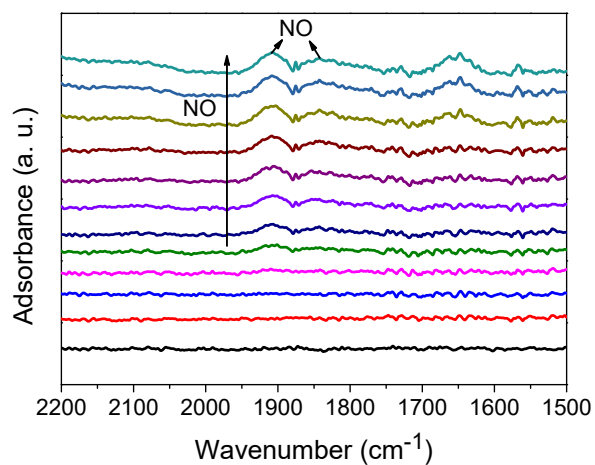


Fig. S4 FTIR spectra of NO adsorbed on PDMS-PEG/SiO₂. The arrow represents the direction of increased pressure of NO.

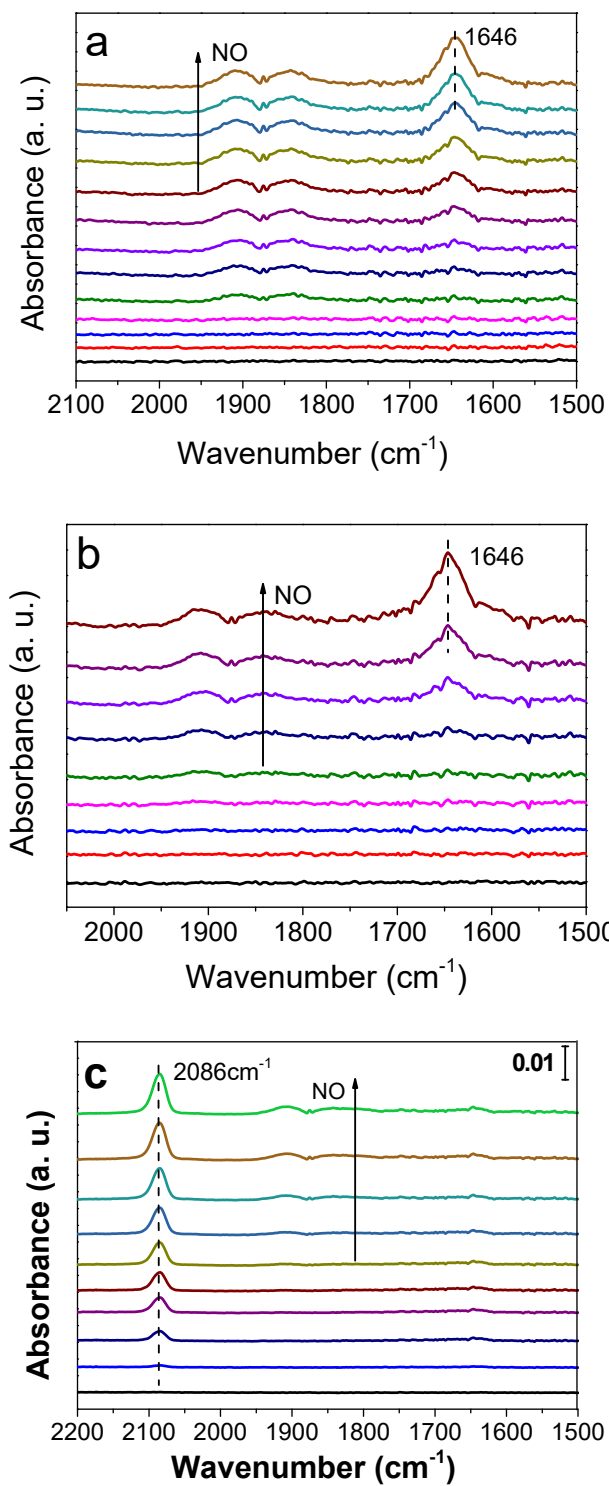


Fig. S5 FTIR spectra of NO on $\text{CuCl}_2@PDMS\text{-PEG/SiO}_2$ (a), $\text{CuCl}_2\text{-Pt@PDMS-PEG/SiO}_2$ (b), $\text{PtCu@PDMS-PEG/SiO}_2$ (c). The arrow represents the direction of increased pressure of NO.

Table S1 Catalytic performance of PtCu@PDMS-PEG, Pt@PDMS-PEG and Karstedt catalyst for hydrosilylation of 1-octene.

$\text{C}_6\text{H}_{13}\text{-CH=CH}_2 \xrightarrow[\text{Cat.}]{(\text{Me}_3\text{SiO})_2\text{MeSiH}} \text{C}_6\text{H}_{13}\text{-CH}_2\text{-CH}_2\text{-SiMe(OSiMe}_3)_2$						
Catalyst	Cat. (mol % to 1-octene)	Tem./ °C	t /min	Conv./%	Yield/%	TOF/h ⁻¹ ^a
PtCu@PDMS-PEG	1×10 ⁻⁴	70	5	72	68	8.64 (± 0.17) ×10 ⁶
			10	97	95	5.82 (± 0.12) ×10 ⁶
Pt@PDMS-PEG	1×10 ⁻⁴	70	15	73	68	2.92 (± 0.06) ×10 ⁶
			20	92	92	2.76 (± 0.06) ×10 ⁶
Karstedt	3×10 ⁻³	72	15	>95	78	1.4×10 ⁵

^a The activity is normalized by the number of Pt atoms