

Electronic Supplementary Information

Synthesis of Platinum Nanoparticles Templated by Dendrimers

Terminated with Alkyl Chains

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1. Nomenclature and Abbreviations

Table S1. Nomenclature and abbreviations

Abbreviation	Name/description
NMR	nuclear magnetic resonance
TEM	transmission electron microscopy
UV-vis	ultraviolet–visible spectroscopy
FT-IR	Fourier-transform infrared spectroscopy
XPS	X-ray photoelectron spectroscopy
PtNPs	Pt nanoparticles
S-DPtNPs	dendrimer-encapsulated platinum nanoparticles with small sizes
L-DPtNPs	dendrimer-encapsulated platinum nanoparticles with large sizes

2. Materials and Methods

Materials

PAMAM dendrimer (ethylenediamine core, generation 4.0, amino surface groups, 10 wt.% in methanol), and dodecyl acrylate (technical grade, 90 %) were purchased from Sigma-Aldrich. Tetraoctylammonium bromide (98 %), and potassium tetrachloroplatinate(II) (98 %) were purchased from Shanghai Macklin Biochemical Co., Ltd. Unless otherwise stated, all chemicals were used as received.

NMR

^1H NMR spectra were recorded on a Varian Inova 600 instrument at 25 °C. Chemical shifts are reported as δ (ppm) values, and residual solvent peaks are chosen as internal standards.

TEM

TEM images were taken on a TECNAI G20 microscope (FEI Inc.) operating at 120 kV. The samples were prepared by dropping the samples dispersed solution onto the carbon-coated copper grids. The solvent was allowed to dry at ambient conditions before observation. At least five different positions were studied for each sample.

FT-IR

FT-IR measurements were conducted on a Nicolet iS50 spectrometer (Thermo Fisher Scientific, USA).

UV-vis

UV-vis spectra were recorded on a MAPADA UV-1800PC spectrometer at room temperature. The scan range was 200-900 nm, and it was corrected against an appropriate background spectrum.

XPS

XPS spectra were recorded on a SPECS system (Germany) equipped with an Al X-ray source, a PHOIBOS 150 analyzer, and an MCD-9 detector. Analysis and fitting of the XPS spectra was performed using XPS PEAK, and the Shirley-type background was used.

3. Synthesis and Characterization of PAMAM-C12

Synthesis of PAMAM-C12

Amine-terminated, fourth-generation PAMAM dendrimer (4.00 g, 10 wt.% in methanol, 1.80 mmol amino surface groups) and dodecyl acrylate (1.60 g, 6.67 mmol) were placed in a round-bottom flask. This solution was stirred and kept at 40 °C for 24 h in air. After cooling to room temperature, a viscous precipitated product was collected by centrifugation (5000 rpm, 10 min) and washed with methanol five times. The product was dried under high vacuum at room temperature. A viscous and transparent PAMAM-C12 (0.51 g) was obtained.

Characterization of PAMAM-C12

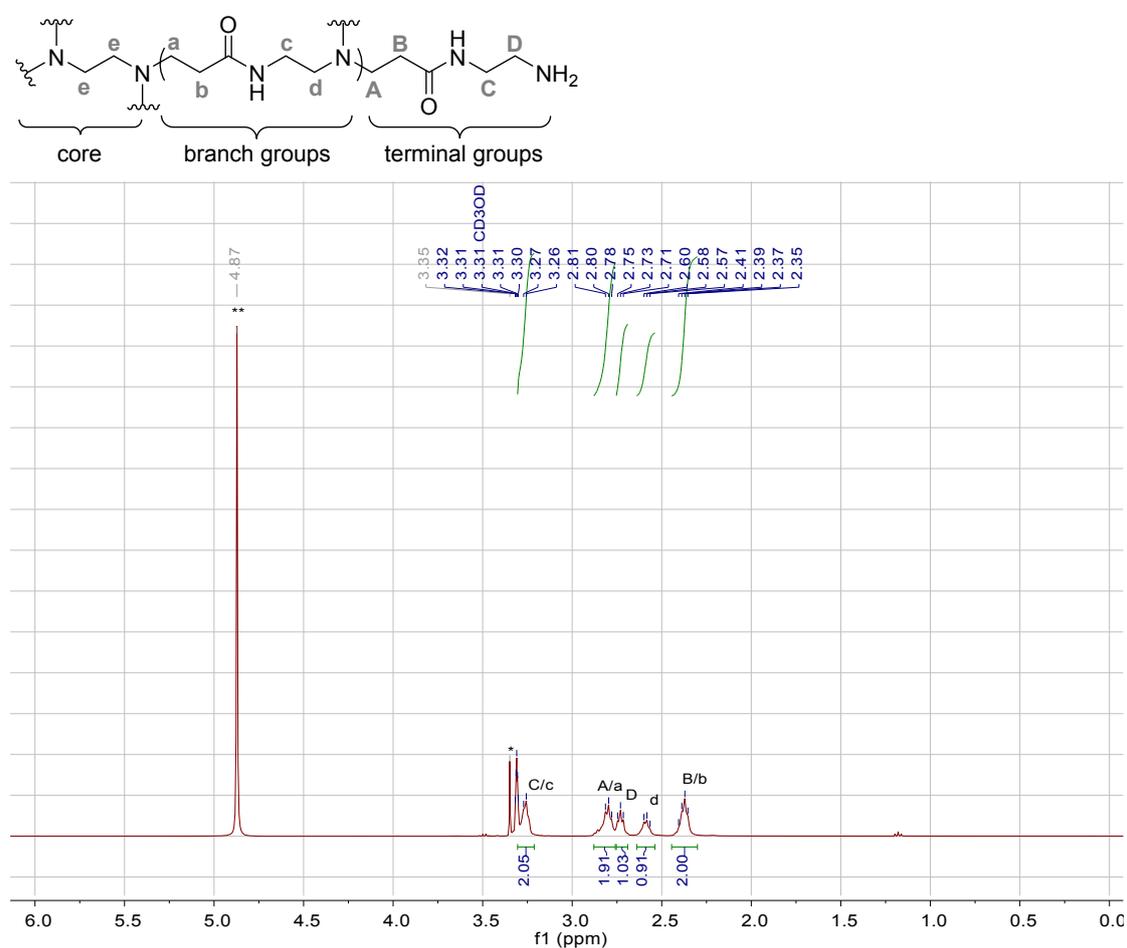


Figure S1. ¹H NMR spectrum of amine-terminated, fourth-generation PAMAM dendrimer in CD₃OD. The peak marked with a single asterisk arises from residual methanol, and the peak marked with a double asterisk arises from water. The assignment of peaks refers to a previous work.¹

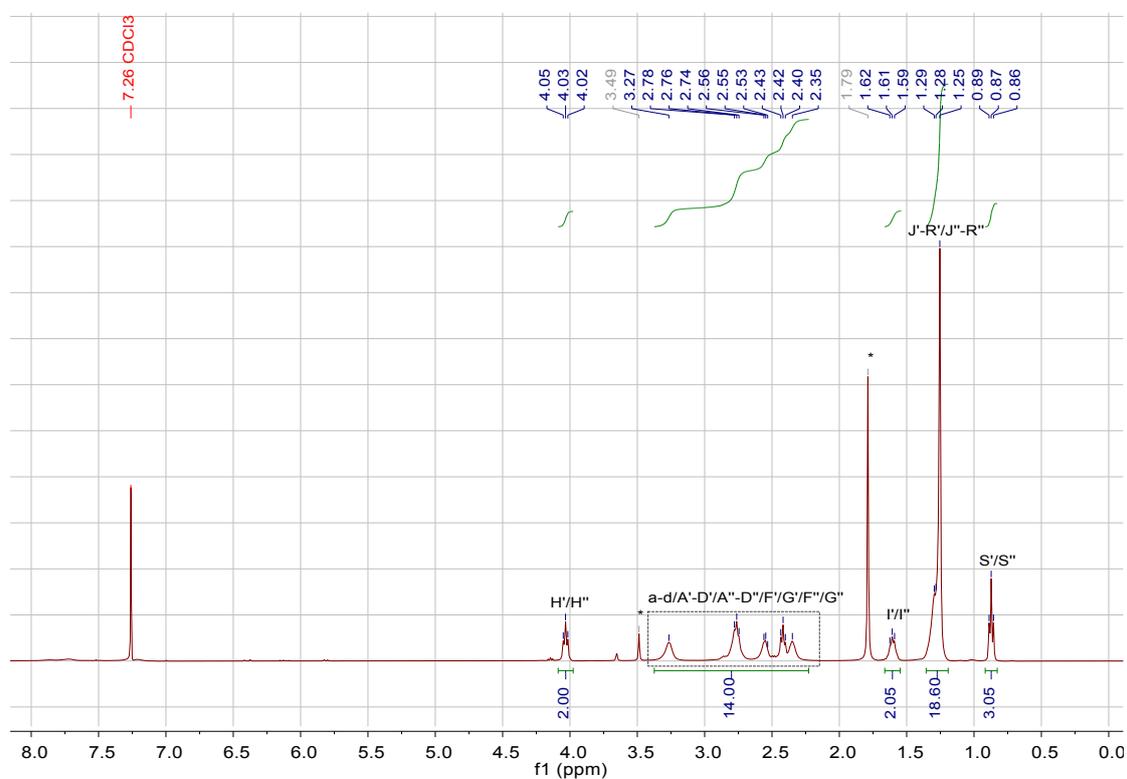
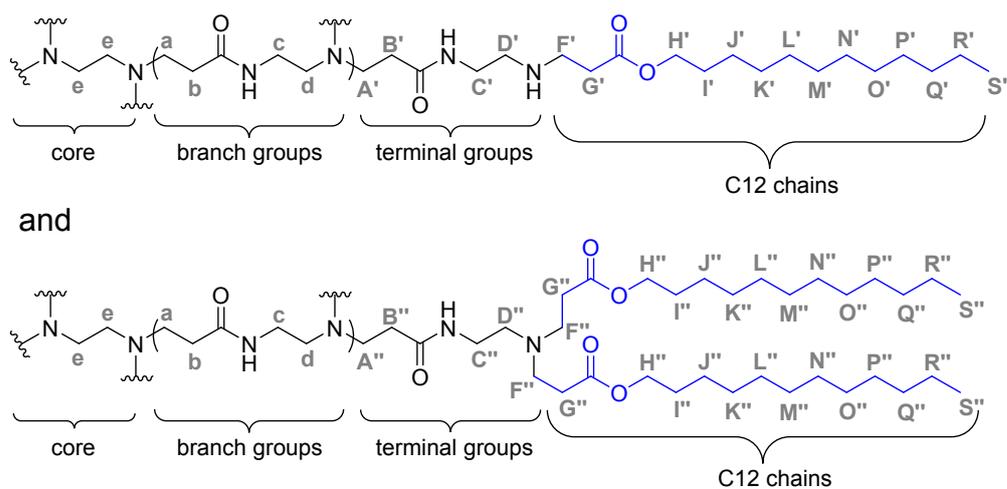


Figure S2. ^1H NMR spectrum of PAMAM-C12 in CDCl_3 . The peaks marked with a single asterisk arise from residual methanol. The number of dodecyl groups was calculated based on the H'/H'' peak and the $\text{a-d}/\text{A}'\text{-D}'/\text{A}''\text{-D}''/\text{F}'/\text{G}'/\text{F}''/\text{G}''$ peaks. Approximate 100 dodecyl groups were attached to the surface of each dendrimer.

4. Synthesis and TEM images of PtNPs

Synthesis of PtNPs templated by PAMAM-C12

Tetraoctylammonium bromide (0.280 g, 0.512 mmol) and PAMAM-C12 (15 mg, 0.378 μmol) were added to toluene (5 mL). K_2PtCl_4 (0.100 g, 0.242 mmol) was added to deionized water (5 mL). The prepared toluene solution and K_2PtCl_4 aqueous solution were mixed in a separating funnel. The toluene phase became dark red, indicating the successful extraction of PtCl_4^{2-} ions from water phase. And the water phase became almost colorless and discarded. The toluene phase was collected and placed in a 10 mL single-neck round-bottom flask, to which trimethylamine (140 μL , 1.00 mmol) was added. The flask was flushed with hydrogen for 10 min to remove residue air and then capped with a rubber septum, on which a hydrogen balloon was applied. The solution was stirred and kept at room temperature for 96 hours. After which, a black solution was obtained. The black solution was washed with an aqueous solution of HCl (1 M), an aqueous solution of sodium carbonate (1 M), an aqueous solution of KBr (1 M), and deionized water. The resulting toluene solution passed an MgSO_4 column (~ 1 cm in height) to remove water and white sediments. The filtrate was added to a methanol solution (30 mL), and then a black solid was precipitated and collected by centrifugation (6000 rpm, 10 min). The black solid was dispersed in hexane (5 mL) and precipitated from methanol to remove tetraoctylammonium bromide. After removing residual methanol, the black solid (**L-DPtNPs-1**) was dispersed in hexane (5 mL) as a stock solution for further use. **L-DPtNPs-2** was synthesized using the same procedure, except 0.500 g of K_2PtCl_4 (1.21 mmol), 1.400 g of tetraoctylammonium bromide (2.56 mmol), 15 mg of PAMAM-C12 (0.378 μmol) and 700 μL of trimethylamine (5.00 mmol) were used.

TEM images of PtNPs

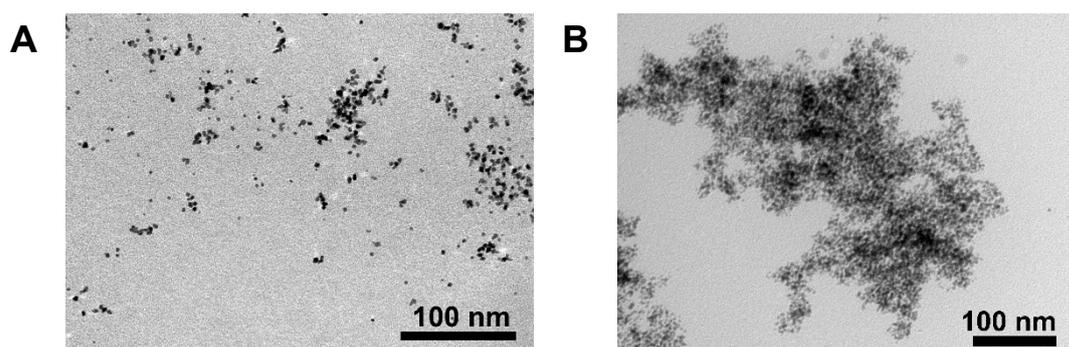


Figure S3. TEM images of (A) L-DPtNPs-1 and (B) L-DPtNPs-2.

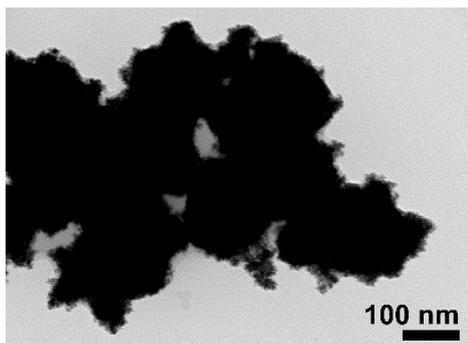


Figure S4. TEM image of precipitates of Pt synthesized in the absence of PAMAM-C12.

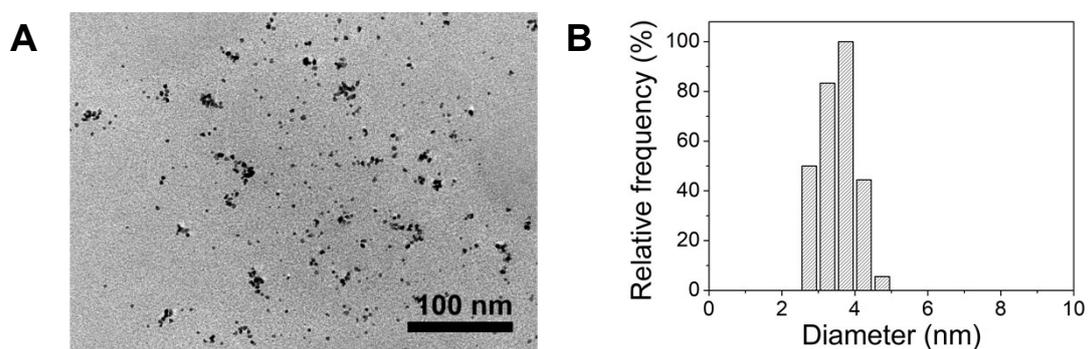


Figure S5. TEM image (A) and the corresponding size distribution (B) of L-DPtNPs with an average size of 3.4 ± 0.5 nm. The molar ratio of PtCl_4^{2-} to PAMAM-C12 was ~ 1000 .

5. References

1. Gomez, M. V.; Guerra, J.; Myers, V. S.; Crooks, R. M.; Velders, A. H., Nanoparticle Size Determination by ^1H NMR Spectroscopy. *J. Am. Chem. Soc.* **2009**, *131* (41), 14634-14635.