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Metallo dendrimers in three oxidation states with electronically interacting metals and stabilization of size-selected gold nanoparticles

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Metallo dendrimers containing redox-robust centres may have applications in molecular redox recognition, sensing, biosensing and catalysis. So far, however, no metallo dendrimer is known in several oxidation states. Here we report metallo dendrimers with two electronically communicating iron centres that are stable and isolated in both the Fe^{II} and Fe^{III} oxidation states, and in addition as class-II mixed-valent Fe^{II}Fe^{III} complexes. These dendrons are branched to arene-centred dendrimer cores either by Sonogashira coupling or 'click' reactions. The latter reaction involves the introduction of intradendritic 1,2,3-triazolyl ligands, which allows investigation of the selective role of these ligands in intradendritic Au^{III} coordination and Au⁰ nanoparticle stabilization. As a result, and using the various metallo dendrimers with different oxidation states, small Au⁰ nanoparticles are intradendritically stabilized by the triazole ligands, whereas with the related non-'click' dendrimers large Au⁰ nanoparticles are formed outside the dendrimers and stabilized by a group of dendrimers.

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To date, dendrimers and metal nanoparticles (NPs) have been largely involved in materials science including nanomedicine, photonics and supramolecular chemistry^{1–5}, and in particular metallo-dendrimers and dendrimer-containing NPs^{2–4,6–11} have been efficiently designed for catalysis^{2–4}, photophysics^{7–11} and sensing^{9–13}. Redox-stable metallo-dendrimers are a specific class of materials allowing redox anion recognition, sensing^{2–16} and biosensing^{14,15} that have been used essentially with ferrocene derivatives^{12–15}. Although biferrocene- and silicon-bridged biferrocene-terminated dendrimers are known^{5,14–16}, no dendrimers have yet been isolated in several oxidation states owing to instability of the odd-electron species. The flexibility of oxidation-state variation with the maintenance of stability for a large collection of metal centres located at the metallo-dendrimer periphery is highly desirable, however, because it would allow the design of nanodevices towards applications in molecular nanoelectronics including nanobatteries¹⁷ and polyelectrolytes¹⁸.

Here we present the synthesis and redox, electronic and NP-stabilization properties of new metallo-dendrimers in three robust oxidation states including mixed-valent metallo-dendrimers. The metal centres located at the dendritic periphery are organized in dendrons in such a way that the two metal centres of the dendrons are electronically communicating. Redox reactions of transition-metal complexes^{19–22} are essential to organize molecular electronic communication in nanomaterials²³. The redox-rich iron centres in the chosen system are $\text{Cp}^*\text{Fe}^{\text{II}}(\text{dppe})$ -alkynyl units ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, $\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$)²⁴ that are isolobal to ferrocene and linked in meta

position of an aryl bridge. In 1,3,5-trimetallaalkynylbenzene derivatives^{24–27}, and in such $\text{Cp}^*\text{Fe}^{\text{II}}(\text{dppe})$ derivatives in particular^{25,26}, it has been shown by density functional theory calculation and electrochemistry that, unlike in the 1,3,5-triferrocenylalkynylbenzene derivatives²⁸, the three metals are electronically communicating. We synthesize the dendrons with only two iron-ethynyl groups in 1,3 position, leaving the third ethynyl position free for binding to the dendritic core either by Sonogashira coupling^{29,30} or copper-catalysed azide-alkyne cycloaddition (CuAAC, ‘click’) reactions^{31–33} with appropriately functionalized dendritic core termini. In this way, metallo-dendrimers in the three oxidation states $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$, $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ and $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}$ are synthetically accessible with and without 1,2,3-triazolyl ligands on the branches, and the latter parameter strongly influences their ability to stabilize and isolate gold NPs (AuNPs) on HAuCl_4 reduction. As a result, we demonstrate how the presence and number of these intradendritic ligands is crucial to form well-defined, very small AuNPs.

Results

Dendron and dendrimer synthesis. Both new bimetallic dendrons **1** and **2** were prepared from the precursor complex $[\text{FeCp}^*(\text{dppe})\text{Cl}]$ according to Fig. 1. Treatment of one equiv. of 1,3,5-triethynylbenzene with two equiv. of $[\text{FeCp}^*(\text{dppe})\text{Cl}]$ and NH_4PF_6 in a methanol/tetrahydrofuran (THF) mixture (1:1), followed by deprotonation with KOBu^t produced 1-ethynyl-3,5-bis(iron)alkynylbenzene, **1**, with 60% yield, and 1-bromo-3,5-bis(iron)alkynylbenzene, **2**, was obtained upon reaction of

Figure 1 | Synthesis of dendrons and dendrimer 3. Reactions of $[\text{FeCp}^*(\text{dppe})\text{Cl}]$ in the presence of NH_4PF_6 with 1,3,5-triethynylbenzene and with 1-bromo-3,5-bis(ethynyl)benzene, both followed by deprotonation with KOBu^t , produced respectively the dendrons **1** and **2**. The hexanuclear compound **3** was obtained in two methods under Sonogashira reactions: (i) Sonogashira reaction between dendron **1** and 1,3,5-triiodobenzene catalysed by $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and CuI and (ii) reaction of dendron **2** with 1,3,5-triethynylbenzene under the same conditions.

[FeCp*(dppe)Cl] with 1-bromo-3,5-bis(ethynyl)benzene in 70% yield (Fig. 1). Both complexes **1** and **2** were isolated as orange microcrystals following standard column chromatography. The characterizations of complexes **1** and **2** are gathered, respectively, in the Supplementary Figs 1–6 and 7–12.

The hexanuclear compound **3** was obtained as deep orange microcrystals using two methods shown in Fig. 1: (i) Sonogashira reaction between dendron **1** and 1,3,5-triiodobenzene catalysed

by [Pd(PPh₃)₂Cl₂] and CuI (Fig. 1) giving **3** with 50% yield and (ii) reaction of dendron **2** with 1,3,5-triethynylbenzene under the same conditions (55% yield). The ³¹P NMR spectrum (C₆D₆) of **3** exhibits a broad signal (99.39 δp.p.m.) due to the steric hindrance in the hexanuclear complex revealing slow rotation on the NMR timescale. The characterizations of the complex **3** are gathered in Supplementary Figs 13–18.

Figure 2 | Syntheses of dendrimers **4 and **5A** by Sonogashira reactions. (a)** The dodecairon complex **4** was synthesized from the Sonogashira reaction between dendron **1** and hexakis(4-iodophenyl)-benzene. **(b)** The *p*-iodophenyl-terminated dendrimer with nine branches was synthesized from the dendritic core 1,3,5-[(CH₂)₃SiMe₂CH₂I]₃-C₆H₃, G0-CH₂I, by Williamson reaction with *p*-iodophenol. These dendritic precursors were then functionalized with dendron **1** according to Sonogashira reaction to give the dendrimer **5A**.

Figure 3 | Syntheses of dendrimer 6A by Sonogashira reaction. The dendrimer **6A** was obtained under the identical strategies with dendrimer **5A** from 27 iodomethylsilyl-terminated analogue G1-CH₂I.

The dodecairon complex **4** was synthesized from the reaction between dendron **1** and hexakis(4-iodophenyl)-benzene catalysed by [Pd(PPh₃)₂Cl₂] and CuI (Fig. 2a). Its infrared spectra show the disappearance of the absorption band around 2,275 cm⁻¹ corresponding to the free alkynyl absorption ($\nu_{\text{C}\equiv\text{C}}$). The characterizations of the complex **4** are gathered in Supplementary Figs 19–24.

From the known dendritic cores 1,3,5-[C(CH₂)₃SiMe₂-CH₂I]₃-C₆H₃, G0-CH₂I, containing 9 terminal iodomethylsilyl branches (Fig. 2b), and the 27 iodomethylsilyl-terminated analogue G1-CH₂I (Fig. 3), azido- (Figs. 4 and 5) and *p*-iodophenyl-terminated (Figs 2 and 3) dendrimers were synthesized with 9 and 27 branches by I/N₃ substitution or Williamson reactions with *p*-iodophenol, respectively. These dendritic precursors were then functionalized with dendron **1**

according to Sonogashira (Figs 2 and 3) and ‘click’ reactions (Figs 4 and 5), respectively. The characterizations of complexes **G0-PhI** and **5A** are gathered in Supplementary Figs 25–27 and 28–33, respectively. Those of complexes **G1-PhI** and **6A** are gathered in Supplementary Figs 34–36 and 37–41, respectively, and those of complexes **5B** and **6B** are gathered in Supplementary Figs 42–47 and 48–53, respectively.

Diffusion-ordered spectroscopy experiments were carried out for the dendrimers **3**, **4**, **5A**, **5B**, **6A** and **6B**. The main goal was to determine the diffusion coefficient *D* leading to the hydrodynamic radii of the dendrimer. The spectra also reflected the purity of the products (the measurements were reproducible). The dendrimer size was found to regularly increase with the increase of the number of Fe(II) units at the dendrimer periphery. Also, the values obtained from

Figure 4 | Syntheses of dendrimer 5B by CuAAC 'click' reaction. Azido-dendrimer with nine branches was synthesized by I/N_3 substitution from the dendritic core 1,3,5- $\{C[(CH_2)_3SiMe_2CH_2I]_3\}_3-C_6H_3$, GO- CH_2I , containing nine terminal iodomethylsilyl. This dendritic precursor was then functionalized with dendron **1** according to 'click' reaction to give the dendrimer **5B**.

dynamic light scattering (DLS) were much larger than the sizes obtained from diffusion-ordered spectroscopy and simulation owing to intermolecular associations³⁴. The data are gathered in Table 1.

The cyclic voltammograms of all the metallodendrons and metallodendrimers (Supplementary Fig. 54) were recorded. They showed two reversible waves around -0.5 and -0.6 V, respectively, with a wave separation (ΔE_p) of 0.11 – 0.13 V for the metallodendrons (Table 2) with a slight solvent effect and only around 0.070 – 0.080 V for the metallodendrimers. For the later, the cyclic voltammogram waves are broad with significant adsorption owing to their large size, which prevents clear wave separation and accuracy in the determination of the potentials, although the comproportionation constants (Table 2) are sufficient for further syntheses of the mixed-valent complexes (*vide infra*).

Synthesis of the oxidized metallodendrimers. Mixed-valent complexes that are indicators of electronic communication between neighbouring redox sites³⁵ are useful tools and models of electronic communication in nanomaterials³⁶. The neutral Fe^{II} metallodendrimers **3**, **4**, **5B** and **6B** have been oxidized in dichloromethane (DCM) to the deep-blue fully oxidized ($Fe^{III}Fe^{III}$) metallodendrimers **3**(PF_6)₆, **4**(PF_6)₁₂, **5B**(PF_6)₁₈, **6B**(PF_6)₅₄ using one equiv. ferricinium hexafluorophosphate ($FcH^+PF_6^-$) per Fe centre. Oxidation to the green mixed-valent metallodendrimers **3**(PF_6)₃, **4**(PF_6)₆, **5B**(PF_6)₉ and **6B**(PF_6)₂₇ was conducted using only one equiv. $FcH^+PF_6^-$ per metallodendron. Alternatively, these mixed-valent metallodendrimers were synthesized on mixing equimolecular amounts of the Fe^{II} metallodendrimers and the fully oxidized Fe^{III} metallodendrimers (Figs 6 and 7). Ferrocene that was formed in these reactions was removed on washing with pentane, and the oxidized metallodendrimers were characterized by Fourier transform infrared (Supplementary Figs 55–70 and Supplementary Table 1), Mössbauer spectroscopies (Supplementary Fig. 71 and Supplementary Table 2), near-infrared (Supplementary Fig. 72 and Supplementary Table 3), ultraviolet–visible (Supplementary Table 4) and elemental analysis.

The infrared spectra of all the multinuclear iron(II) and iron(III) complexes display a single $C\equiv C$ stretching band around $2,040$ and $2,000\text{ cm}^{-1}$, respectively (Supplementary Table 1). In contrast, the infrared spectra of all the mixed-valent complexes show two distinct $C\equiv C$ stretching bands at these wavenumbers, providing evidence for localized oxidation states at 10^{13} s^{-1} . The Mössbauer spectra of all the mixed-valent complexes recorded at 78 K show two quadrupole doublets of approximately equal intensities corresponding to the Fe^{II} and Fe^{III} states (Supplementary Table 2), indicating localized mixed valency at 10^{-7} s^{-1} . The intervalence charge transfer (IVCT) band (Supplementary Table 3) of the four mixed-valent complexes was found in the near-infrared region in CD_3COCD_3 . The full width at half height of the band is very close to the theoretical value derived from the near-infrared band position λ_{max} according to Hush's relationship for symmetrical mixed-valent complexes. The ratios $(\Delta\nu_{1/2})_{obs}/(\Delta\nu_{1/2})_{calc}$ were less than 1.15, falling in the 1.1–1.4 range of class-II mixed-valent complexes^{36–38}. The UV-vis spectra of all the multinuclear complexes (Supplementary Table 4) display intense absorption bands in the range 250–380 nm (LC $\pi-\pi^*$ transition) and around 400 nm (metal to ligand charge transfer (MLCT) transition) responsible for the orange colour of the neutral compounds and also present in the deep colour of the mixed-valent/fully oxidized products, whereas the oxidized complexes present two transitions above 550–580 and 645–680 nm explaining their green/blue colour³⁸. The mixed-valent properties of all the mixed-valent dendrimers are further discussed in the Supplementary Notes 1–5.

Stabilization of AuNPs. The availability of metallodendrimers in three oxidation states with 54 $Cp^*Fe(dppe)alkynyl$ termini with interiors containing or not 1,2,3-triazole ligands offered the opportunity to examine the influence of the intradendritic presence of these triazole ligands on the stabilization of AuNPs^{39–42}. Indeed, it was possible to start either from $Fe^{II}Fe^{II}$ metallodendrimers to reduce Au^{III} into AuNPs (equation (1)) or from $Fe^{III}Fe^{III}$ metallodendrimers and Au^{III} and to reduce the mixture using excess $NaBH_4$ to $Fe^{II}Fe^{II}$ and AuNPs (equation (2)). These experiments were conducted with the

Figure 5 | Syntheses of dendrimer 6B by CuAAC ‘click’ reaction. The dendrimer **6B** was obtained under the identical strategies with dendrimer **5B** from 27 iodomethylsilyl-terminated analogue G1-CH₂I.

dendrimer **6A** and **6B** and with dendron **1** for comparison, and the results are gathered in Table 3 and Supplementary Figs 73–82.

The AuNPs formed from **6A** gave a much more intense plasmon absorption in the ultraviolet–visible spectrum than **6B** around 530 nm indicating much larger AuNPs (Fig. 8). Accordingly, the

smallest AuNPs (cores: 1.4 and 1.9 nm from equation (1) resp. equation (2)) were obtained with the ‘click’ metallodendrimer **6B**. The Sonogashira metallodendrimer **6A** gave larger AuNPs (cores: 3.4 and 3.7 nm from equation (1) resp. equation (2)), and the metallodendrimer **1** gave large AuNPs with equation (1) (20 nm core), but small AuNPs (2 nm core) according to equation (2) (Fig. 9).

Discussion

In this work, the syntheses and characterizations of metallodendrimers in three oxidation states have been achieved for the first

time, allowing redox interplay exemplified by the formation of AuNPs of selective size depending on the presence and number of intradendritic 1,2,3-triazole ligands.

The metallodendrimers have been designed using interacting metal centres in new bimetallic dendrons. It is the electronic communication between these two iron centres within each bimetallic dendron that provides the occurrence of another stable oxidation state that is class-II mixed-valent in the Robin–Day classification as shown by the splitting of the $C\equiv C$ stretching band in infrared and presence of a near-infrared intervalent band.

The choice of the method of dendron connection to dendrimer cores, Sonogashira versus ‘click’ reaction, further results in the

Table 1 | Size parameters.

Compound	D (Diffusion coefficient) (± 0.01) $\times 10^{-10} \text{ m}^2 \text{ s}^{-1}$	r_H (Hydrodynamic radius from DOSY) (± 0.1) nm	D_H (Hydrodynamic diameter from DLS) (nm)	D (Chemdraw simulation) (nm)
3	0.93	3.6	55 ± 5	2.0 ± 0.2
4	0.73	4.6	102 ± 10	2.6 ± 0.2
5A	0.59	5.7	54 ± 2	3.6 ± 0.3
5B	0.55	6.1	39 ± 2	3.3 ± 0.3
6A	0.35	9.6	37 ± 4	5.4 ± 0.5
6B	0.40	8.4	99 ± 10	5.1 ± 0.5

DOSY, diffusion-ordered spectroscopy.

Figure 6 | Oxidation of metallodendrimers. Oxidation of the metallodendrimer **3** to the mixed-valent dendrimer $3(\text{PF}_6)_3$ and fully oxidized dendrimer $3(\text{PF}_6)_6$. The Fe^{II} species are in red and the Fe^{III} species are in blue.

Figure 7 | Oxidation of metallogeniters. (a–c) The following mixed-valent metallogeniters **4**(PF₆), **5B**(PF₆)₉ and **6B**(PF₆)₂₇ have been obtained analogously. The Fe^{II} species are in red and the Fe^{III} species are in blue.

presence or absence of ‘clicked’ 1,2,3-triazolyl intradendritic ligands. This dendrimer engineering providing electronic flexibility is unique in that the stability and isolation of different dendrimer oxidation states allow examining the influence of the presence and number of these triazole ligands on the intradendritic coordination of Au^{III} moieties. As a consequence, it could be shown here that the intradendritic AuNP stabilization specifically induces the formation of small AuNPs.

The results are well taken into account by coordination of Au³⁺ by the triazole ring in both equations (1) and (2) experiments followed by reduction to small monodisperse AuNPs (1.4 ± 0.3 nm) having a core size slightly higher than 27 Au atoms inside a dendrimer, owing to some leaching of Au atoms among dendrimers (the diameter of a 27-atom AuNP is 1 nm). The triazole loosely interacts with the AuNP surface, which contributes to its intradendritic stabilization of these small AuNPs.

Table 2 | Compared $E_{1/2}$ and comproportionation constant values.

Compound	$E'_{1/2}$ (V)	$E''_{1/2}$ (V)	ΔE_{ox} (mV)	K'_{com}
1 *	−0.50	−0.63	130	158
1 [†]	−0.42	−0.53	110	72
2 *	−0.50	−0.63	130	158
3 [†]	−0.44	−0.54	100	49
4 *	−0.51	−0.63	120	106
5A [†]	−0.45	−0.53	80	23
5B [†]	−0.46	−0.53	70	15
6A [†]	−0.45	−0.53	80	23
6B [†]	−0.46	−0.53	70	15

K'com, comproportionation constant.

(Cyclic voltammogram using [*n*-Bu₄N][PF₆] as the supporting electrolyte at 293 K; working and counter electrodes: Pt; reference electrode: Ag; scan rate: 0.200 V s^{−1} versus FeCp₂ under the same concentration (2 mM).*In CH₂Cl₂.

†In THF.

Figure 8 | Compared ultraviolet-visible absorption spectra in CH₂Cl₂. The AuNPs stabilized by reaction of NaBH₄ with a mixture of HAuCl₄ and dendron **1** [PF₆]₂ (blue line), **6A** [PF₆]₅₄ (black line) or **6B** [PF₆]₅₄ (red line) under identical conditions giving back the neutral dendrimers (equation (2)).**Table 3 | Properties of AuNPs prepared by the methods of equations (1) and (2).**

Method	Start	Final	Final colour	Core size (TEM, nm)	Overall size (DLS, nm)*	Plasmon band (nm) [†]
Equation (1)	1	1 ⁺	Dark green	20.2 ± 3	—	516
	6A	6A ²⁷⁺	Dark green	3.3 ± 0.5	—	514
	6B	6B ²⁷⁺	Dark green	1.4 ± 0.3	—	537
Equation (2)	1 ²⁺	1	Violet	2.0 ± 0.3	75 ± 3	515
	6A ⁵⁴⁺	6A	Violet	3.7 ± 0.5	111 ± 5	525
	6B ⁵⁴⁺	6B	Deep violet	1.9 ± 0.3	113 ± 5	545

TEM, transmission electron microscopy.

The data were obtained by reducing of the Fe^{II}Fe^{III} dendrimers to neutral Fe^{II}Fe^{II} dendrimers using NaBH₄.

*DLS of AuNPs synthesized by method of equation (1) is not available owing to the ionic structures.

†The plasmon band of AuNPs obtained by the method of equation (1) is hidden by the ligand-metal charge-transfer band (LMCT) of the mixed-valent metallodendrimer.

Figure 9 | Schematic picture representing the AuNP stabilized by dendrimers. (a) Intradendritic AuNP stabilization by a 'click' dendrimer **6B**²⁷⁺ involving AuNP-triazole interactions. (b) Interdendritic stabilization by many 'Sonogashira' dendrimers **6A**²⁷⁺. It is likely that chloride anions surround the AuNPs in both cases.

Figure 10 | Transmission electron microscopy of AuNPs. AuNPs stabilized by reaction of NaBH_4 with a mixture of HAuCl_4 and dendron **1** [PF_6]₂ (**a** and **b**), **6A** [PF_6]₅₄ (**c** and **d**) or **6B** [PF_6]₅₄ (**e** and **f**) under identical conditions giving back the neutral dendrimers. Scale bars; **a** and **c**, 100nm; **a** (inset) and **c** (inset), 20 nm; **e**, 50 nm.

On the contrary, the larger AuNPs stabilized by the Sonogashira dendrimer **6B** gather a number of atoms around 1,400, which involves considerable distribution around dendrimer peripheries and final stabilization of each AuNP by several dendrimers, because Au^{III} reduction essentially proceeds outside dendrimers, and there are no heteroatom-containing ligand retaining AuNPs inside the dendrimers (Fig. 10). The small dendrons allow the formation of a very large AuNP core surrounded by a large number of dendrons because small dendrons are much less efficient than large dendrimers for NP stabilization.

Remarkably, the AuNP core size of the Au^{III} -‘click’-dendrimer complexes does not vary considerably with the mode of formation for the dendrimers **6A** and **6B** whatever the synthetic route (equation (1) versus equation (2)). Indeed, the AuNP core size approximately corresponds to the number of Au atoms generated from the triazolyl-coordinated Au^{III} precursors in a single dendrimer. It does for dendron **1**, however, because AuNP stabilization by borohydride then predominates in equation (2) in the absence of strong dendritic stabilization.

On the other hand, the related non-‘click’ (Sonogashira) dendrimers generate much larger AuNPs formed outside the metallodendrimers, but also stabilized by a group of metallo-dendrimers around the AuNP (Supplementary Notes 6 and 7). Such a nanomaterial engineering strategy should be most useful for the design of sophisticated nanosensors, nanocatalysts, nanobatteries and nanopolyelectrolytes in the near future⁶.

Methods

Synthesis and characterizations of dendron 1. 1,3,5-Triethynylbenzene (150 mg, 1 mmol) in 10 ml distilled THF was added to a solution of $[\text{FeCp}^+(\text{dppe})\text{Cl}]$ (1.56 g, 2.5 mmol) and NH_4PF_6 (326 mg, 2 mmol) in 12 ml CH_3OH . The suspension was stirred at room temperature (r.t.) for 16 h. The solvent was evaporated *in vacuo*. The residual solid was dissolved in 5 ml distilled DCM, 100 ml distilled pentane was added and the precipitation was washed with pentane for another two times. The residual solid was dissolved in 10 ml distilled THF, and then potassium *tert*-butoxide (224 mg, 2 mmol) was added in a single portion. The mixture was stirred 3 h under r.t., the solvent was removed *in vacuo* and the residue was extracted with distilled diethylether to form the crude compound that was further purified by column chromatography (pentane/diethylether = 5/1, R_f = 0.2) providing dendron **1** as an orange powder (795.6 mg, yield = 60%). Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF): calc. m/z for M^+ ($\text{C}_{84}\text{H}_{82}\text{Fe}_2\text{P}_4$) 1,327.1, found 1,326.4. Anal. calcd. for $\text{C}_{84}\text{H}_{82}\text{Fe}_2\text{P}_4$: C, 76.02; H, 6.23. Found: C, 76.32; H, 6.38. For dendron **2**, a similar procedure was used. See Supplementary Methods for remaining syntheses; full characterization of all other complexes are not described herein.

Synthesis of dendrimer 6A using a Sonogashira reaction. A mixture of dendron **1** (121 mg, 1.5 equiv. for each branch), G1-PhI (25 mg, 1 equiv. for each branch) and catalytic amount of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (8.5 mg, 0.2 equiv. for each branch) and CuI (4.6 mg, 0.1 equiv. for each branch) were dissolved in the mixed solvent of distilled diisopropylamine (DIPA)/THF 10 ml. The solution was stirred overnight at 50 °C under N_2 . The solvent was evaporated *in vacuo*. The residual solid was extracted with PhCH_3 30 ml, the solution was dried with anhydrous Na_2SO_4 , the solvent was removed *in vacuo* and the dark red residue was washed three times with distilled diethyl ether 50 ml to remove the excess free ligand. Then the residual solid was dissolved in 1 ml of dry THF, 100 ml of dry CH_3CN was added to the mixture and compound **6A** precipitated as a deep orange solid (66 mg, yield = 70%). Anal. calcd. for $\text{C}_{2718}\text{H}_{2838}\text{Fe}_{54}\text{P}_{108}\text{Si}_{36}\text{O}_{36}$: C, 75.13; H, 6.58. Found: C, 75.44; H, 6.47.

Synthesis of dendrimer 6B by 'click' reaction. To a mixture of G1-N₃ (20 mg, 3.6×10^{-3} mmol, 1 equiv.) and dendron 1 (193 mg, 0.146 mmol, 1.5 equiv. for each branch) in THF 20 ml, 10 ml of distilled H₂O was added dropwise, and a solution of CuSO₄ · 5 H₂O (36.5 mg, 0.146 mmol, 1.5 equiv. for each branch) in 1 ml of H₂O was slowly added to the mixture at 0 °C, which provoked a colour change from orange to dark brown. The solution of sodium ascorbate (57.8 mg, 0.292 mmol, 3 equiv. for each branch) was dropwise added to this mixture at 0 °C, which resulted in a colour change from dark brown to orange. Stirring was continued at 50 °C under N₂ for another 16 h, the solvent was evaporated *in vacuo* until only the aqueous phase was left, 50 ml of toluene, 50 ml of H₂O and 3 ml of ammonium hydroxide was added to the solution and the mixture was stirred at r.t. for 30 min for extraction of the Cu catalyst. After separation, the organic phase was dried with anhydrous Na₂SO₄, and the solvent was removed *in vacuo*, which gave a deep orange solid that was washed three times with 300 ml diethyl ether to remove the excess free ligands. This procedure yielded the 'click' dendrimer as an orange solid (89.2 mg, 60%). Anal. calcd. for C₂₅₅₆H₂₇₅₇Fe₅₄P₁₀₈N₈₁O₉Si₃₆: C, 72.87; H, 6.60; N, 2.69. Found: C, 72.69; H, 6.40; N, 2.45. The synthesis and characterizations of 5B were conducted under similar conditions.

Oxidation of the complex 6B to 6B(PF₆)₂₇. The dendrimer 6B (82 mg, 2×10^{-3} mmol, 1 equiv.) was dissolved in 5 ml distilled DCM, and [FeCp₂] [PF₆] (17.7 mg, 0.0535 mmol, 27 equiv.) was added in a single portion to this solution at r.t., which provoked an immediate colour change from orange to dark green, the solution was stirred for 4 h at r.t. under N₂, the solvent was removed *in vacuo* until 0.5 ml was left, then 50 ml of distilled pentane was added to this dark green solution and the mixed-valent dendrimer was precipitated. After filtration, the residual solid was washed twice more with 100 ml pentane, and the residue was dried under vacuum to give the mixed-valent dendrimer as a dark solid (80.9 mg, 90% yield). Anal. calcd. for C₂₅₅₆H₂₇₅₇Fe₅₄P₁₀₈N₈₁O₉Si₃₆(PF₆)₂₇: C, 66.68; H, 6.04; N, 2.46. Found: C, 66.77; H, 6.20; N, 2.45. The oxidation of 3, 4, 5B and 6B by [FeCp₂] [PF₆] to the mixed-valent or fully oxidized dendrimers were conducted identically.

Synthesis of AuNPs stabilized by dendrimer 6B²⁷⁺. The neutral dendrimer 6B (10 mg, 2.419×10^{-4} mmol, 1 equiv. per branch) was dissolved in 2 ml DCM, and the solution of HAuCl₄ (0.86 mg, 2.175×10^{-3} mmol, 1/3 equiv.) in 2 ml of acetone was slowly added to the mixture at r.t., which provoked a colour change from orange to deep green. Stirring was continued for another 30 min. Infrared (KBr): 2,036 cm⁻¹ (ν_{C≡C-Fe(II)}), 2,009 cm⁻¹ (ν_{C≡C-Fe(III)}). Ultraviolet-visible: λ_{max 1} = 410 nm (ν_{II-III}), λ_{max 2}/λ_{max 3} = 580/665 nm (ν_{LMTCT}). Transmission electron microscopy: 1.4 ± 0.3 nm. The synthesis and characterizations of AuNPs stabilized by ionic mixed-valent dendron 1⁺ or dendrimer 6A²⁷⁺ were analogous.

Synthesis of AuNPs stabilized by neutral dendrimer 6B. The neutral dendrimer 6B (5 mg, 1.15×10^{-4} mmol, 1 equiv.) was dissolved in 2 ml of DCM, and [FeCp₂] [PF₆] (2.1 mg, 6.22×10^{-3} mmol, 54 equiv) was added under stirring, which resulted in an instantaneous colour change from orange to deep blue, and the mixture was stirred at r.t. during 4 h. Then, the solvent was removed *in vacuo* until 0.5 ml was left, 50 ml of distilled pentane was added to the mixture and the fully oxidized complex precipitated as a dark product. After filtration, this solid was dried under vacuum, dissolved in 2 ml of distilled DCM and a solution of HAuCl₄ (1 mg, 2.54×10^{-3} mmol) in 2 ml methanol was added to the mixture under stirring, forming a blue solution. Then, a solution of NaBH₄ (2.35 mg, 6.2×10^{-2} mmol, three equiv.) in 1 ml methanol was added dropwise under stirring, leading to a colour change from dark blue to deep violet, which indicated the formation of the AuNPs. The mixture was stirred at r.t. for another 10 min. Infrared (KBr): 2,045 cm⁻¹ (ν_{C≡C-Fe(II)}). Ultraviolet-visible: λ_{max 1} = 410 nm (ν_{II-III}), λ_{max 2} = 545 nm (plasmon band). Transmission electron microscopy: 1.9 ± 0.3 nm. The synthesis and characterizations of AuNPs stabilized by the neutral dendron 1 or the dendrimer 6A were conducted analogously.

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Author contributions

Y.W. and D.A. conceived and designed the experiments and wrote the paper. Y.W. performed the experiments. Y.W. and J.R. conducted the electrochemical measurements. L.S. conducted Mössbauer and transmission electron microscopic experiments.

Additional information

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