

## Electronic Supplementary Information Available

### Assembly Between Gold-thiolate Nanoparticles and the Organometallic Cluster [CpFe( $\mu_3$ -CO)]<sub>4</sub> toward Redox Sensing of Oxo-anions.

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General data, experimental procedures for the syntheses of **2**, **3** and **4** from **1**, and titration graph of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> by **4**, in CH<sub>2</sub>Cl<sub>2</sub>.

#### General data:

All the solvent purifications and reactions were carried out under a purified nitrogen atmosphere. Reagent-grade tetrahydrofuran (THF), diethyl ether, and pentane were predried over Na foil and distilled from sodium-benzophenone anion immediately prior to use. Acetonitrile (CH<sub>3</sub>CN) was stirred overnight over phosphorus pentoxide, distilled from sodium carbonate, and stored under argon. Methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) was distilled from lithium aluminum hydride, methanol was distilled from magnesium, NEt<sub>3</sub> was distilled from LiAlH<sub>4</sub> just before use. The Fe<sub>4</sub> cluster **1** and acid **5** was synthesized according to a procedure reported by Rauchfuss.<sup>17a</sup> All other chemicals were used as received. All manipulations were carried out using Schlenk techniques or in a nitrogen-filled Vacuum Atmosphere Corporation drylab. Infrared spectra were recorded with a Perkin-Elmer 1420 infrared spectrophotometer that was calibrated with polystyrene. Samples were examined in solution (0.1 mm cells with NaCl windows), between NaCl disks in Nujol, or in KBr pellets. <sup>1</sup>H NMR spectra were recorded at 25°C with a Bruker AC 250 (250 MHz) spectrometer. <sup>13</sup>C NMR spectra were obtained in the pulsed FT mode at 62.91 MHz with a Bruker AC 250 spectrometer. All chemical shifts are reported in parts per million ( $\delta$ , ppm) with reference to Me<sub>4</sub>Si (TMS). Elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon-Villeurbanne, France.

**Titration using cyclic voltammetry: common conditions:**

Solvent: distilled CH<sub>2</sub>Cl<sub>2</sub>; temperature: 20 °C; supporting electrolyte: [*n*-Bu<sub>4</sub>N] [PF<sub>6</sub>], 0.1 M; internal reference: FeCp<sub>2</sub>\*; reference electrode: Ag; auxiliary and working electrodes: Pt; scan rate: 0.2 V/s; anion concentration ([*n*-Bu<sub>4</sub>N][H<sub>2</sub>PO<sub>4</sub>] or [*n*-Bu<sub>4</sub>N]<sub>2</sub>[ATP]): 5.10<sup>-3</sup> M; concentration of [*n*-Bu<sub>4</sub>N]Cl and [*n*-Bu<sub>4</sub>N][HSO<sub>4</sub>]: 5.10<sup>-2</sup> M.

Decamethylferrocene, FeCp\*<sub>2</sub>, is used as an internal reference in the CVs in order to avoid overlap with the CV wave of the Fe<sub>4</sub> cluster and for a better accuracy than with ferrocene, FeCp<sub>2</sub>, as a reference.<sup>1</sup> Values of the potentials can be converted vs. the ferrocene reference in CH<sub>2</sub>Cl<sub>2</sub>, however, by subtracting 0.545 V.

**[Fe<sub>4</sub>(μ<sub>3</sub>-CO)<sub>4</sub>Cp<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>COCl)], 6.** A solution of **[Fe<sub>4</sub>(μ<sub>3</sub>-CO)<sub>4</sub>Cp<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>COOH)]**,<sup>17a</sup> **5**, (0.200 g, 0.310 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was treated with oxalyl chloride (0.078 g, 0.620 mmol) at 0 °C. The green solution was allowed to warm up to room temperature, and the solvent was removed under high vacuum. The green powder obtained was used without any further purification.

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ 5.10 (t, 2H), 4.95 (t, 2H), 4.87 (s, 15H). <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>): δ 126.24 (C<sub>5</sub>H<sub>4</sub>), 118.90 (C<sub>5</sub>H<sub>5</sub>), 113.82 (C<sub>5</sub>H<sub>4</sub>).

IR (KBr, cm<sup>-1</sup>): ν<sub>COCl</sub> 1764, ν<sub>FeCO</sub> 1635.

*E*<sub>1/2</sub> (V vs. FeCp<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>; 20 °C): 0.830 (rev.); 0.140 (rev.); -1.505 (rev.); -1.635 (rev.).

**[Fe<sub>4</sub>(μ<sub>3</sub>-CO)<sub>4</sub>Cp<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>CONH(CH<sub>2</sub>)<sub>11</sub>S)]<sub>2</sub>, 7.** A stirred solution of **[Fe<sub>4</sub>(μ<sub>3</sub>-CO)<sub>4</sub>Cp<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>COCl)], 6**, (0.083 g, 0.125 mmol) and of the disulfide [-S-(CH<sub>2</sub>)<sub>11</sub>NHCl]<sub>2</sub> (0.025 g, 0.053 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). Triethylamine (0.023 mL, 0.3 mmol) was added. After 15h, the solvent was removed under vacuum. The residue was re-dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and washed successively with water, saturated sodium carbonate and water again. The organic solution was dried over sodium sulphate, and the solvent was removed under vacuum to give 0.065 g of dark-green powder (63% yield). Anal. Calcd. for C<sub>72</sub>H<sub>84</sub>Fe<sub>8</sub>N<sub>2</sub>O<sub>10</sub>S<sub>2</sub>: C 52.46, H 5.13; found C 51.92, H 5.14.

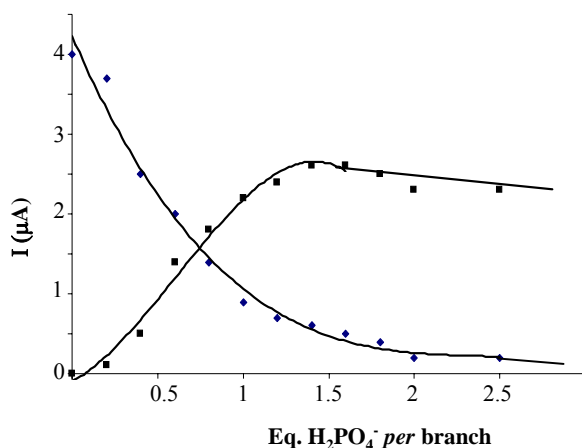
<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ 6.85 (m, 2H), 4.87 (m, 4H), 4.79 (m, 34H), 3.43 (m, 4H), 2.68 (t, 4H) 1.66-1.29 (40H). <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>): δ 109.51 (C<sub>5</sub>H<sub>4</sub>), 99.22 (C<sub>5</sub>H<sub>5</sub>), 98.65 (C<sub>5</sub>H<sub>4</sub>), 39.63 (CH<sub>2</sub>N), 39.20 (CH<sub>2</sub>S), 29.58-27.03 (CH<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): ν<sub>NH</sub> 3351, ν<sub>FeCO</sub> and ν<sub>CON</sub> 1633. *E*<sub>1/2</sub> (V vs. FeCp<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>; -10 °C) = 0.840 (rev.); 0.110 (rev.); -1.620 (rev.)

**Reduction of  $[\text{Fe}_4(\mu_3\text{-CO})_4\text{Cp}_3((\eta^5\text{-C}_5\text{H}_4\text{CONH}(\text{CH}_2)_{11}\text{S}))_2]$  **7** to the thiol **2**.** The cluster oxidized by air to disulfide (0.060 g, 0.036 mmol) was dissolved with 10 mL of DMF in a Schlenk flask. Water (70  $\mu\text{L}$ , 100 equiv.) was added, then the reaction mixture was degassed, tris-*n*-butylphosphine (100  $\mu\text{L}$ , 10 equiv.) was introduced, and the mixture was stirred at room temperature for 3 hours. Then, 50 mL of ethyl acetate was added, and the mixture was washed with HCl 1N. The organic layer was separated, degassed, dried under  $\text{Na}_2\text{SO}_4$  and filtered. The solvent was then removed under vacuum, and the solid residue was rinsed under positive nitrogen pressure using degassed petroleum ether. The green solid thiol (0.055 g, 0.067 mmol, 88%) was dried under vacuum. This procedure was applied for the thiol synthesis just before the synthesis of the cluster-AuNPs.

**Direct Schiffrin-Brust AuNP synthesis.** A colorless solution of  $\text{N}(n\text{-C}_8\text{H}_{17})_4\text{Br}$  (0.524 g, 0.959 mmol) in 10 mL toluene was added to a yellow water solution (10 mL) of  $\text{HAuCl}_4$  (0.093 g, 0.274 mmol). The mixture was stirred under positive nitrogen pressure, resulting in separation between the red organic phase (top) and colorless aqueous phase (bottom). A mixture of dodecanethiol  $\text{C}_{12}\text{H}_{25}\text{SH}$  (0.020 g, 0.100 mmol) and green clusterthiol **4** (0.082 g, 0.100 mmol) in 10 mL of toluene was added to the organic phase. Then,  $\text{NaBH}_4$  (0.100 g, 3.04 mmol) in 10 mL water was slowly added to the stirred reaction mixture. The red color turned to black brown, and the reaction mixture was vigorously stirred for 3 hrs. The organic phase was separated from the aqueous phase, its volume was reduced to 3 mL, and 100 mL ethanol was added. The mixture was kept at  $-20^\circ\text{C}$  for 12 hrs, the resulting dark brown-black precipitate was filtered on celite, then washed with ethanol and acetone to remove excess thiol. The crude product was dissolved in  $\text{CH}_2\text{Cl}_2$  and precipitated again with methanol, then dried under vacuum, which gave 0.085 g of dark-forest-green AuNPs **15** containing the mixture of ligands  $\text{C}_{12}\text{H}_{25}\text{S}/\text{clusterthiol} = 52/48$  (ratio determined by  $^1\text{H}$  NMR). Elemental analysis: S 3.38, Au 45.55; atomic ratio Au/S = 2.2. HRTEM : average diameter =  $1.61 \pm 0.4$  nm. Number of gold atoms *per* core : 101. Number of ligands;  $n = 58$ . Proportion of clusterthiol = 48 %. Average number of cluster-thiolate *per* particle  $n_{\text{clusterthiolate}} = 28$ ;  $n_{\text{alkylthiolate}} = 30$ . MW = 83069 g/Mol.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.01 (br. H, amide); 4.79 (br. H, Cp); 3.39 (br. H, CHN); 1.81, 1.64, 1.27 (br. H, alkylthiol); 0.89 (br. H,  $\text{CH}_3$  alkylthiol).  $^{13}\text{C}$  NMR (76 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 164.18(CON); 106.56 ( $\text{C}_5\text{H}_4$ ); 99.02 ( $\text{C}_5\text{H}_5$ ); 95.94 ( $\text{C}_5\text{H}_4$ ); 31.65 ( $\text{CH}_2$  alkylthiol); 22.68 ( $\text{CH}_2$  alkylthiol); 14.27 ( $\text{CH}_3$  alkylthiol). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{FeCO}}$  and  $\nu_{\text{CON}}$  1634.  $E_{1/2}$  (V vs.  $\text{FeCp}_2$ ;  $\text{CH}_2\text{Cl}_2$ ;  $20^\circ\text{C}$ ) = 0.730 (rev.); 0.045 (rev.); -1.700 (rev.).

**Ligand substitution in alkylthiol-gold nanoparticles.** A  $\text{CH}_2\text{Cl}_2$  (20 mL) solution of undecanethiolthiol-AuNPs<sup>14]</sup> (0.080 g,  $10^{-6}$  mmol) and  $[\text{Fe}_4(\mu_3\text{CO})_4\text{Cp}_3(\eta^5\text{-C}_5\text{H}_4\text{CONH}(\text{CH}_2)_{11}\text{SH})]$ , **7**, was stirred under positive nitrogen pressure at room temperature. After three days, the solvent was evaporated under reduced pressure. The dark-brown product was washed three times with 10 mL methanol, then three times with 10 mL acetone in order to remove the non-coordinated thiols, the desired AuNPs being not soluble in these two solvents (the solvent washing was finally colorless). The black solid was dried under vacuum, giving 0.040 g that contains 7% of substituted functional thiolate ligand in alkylthiol-AuNPs (ratio determined by  $^1\text{H}$  NMR). Elemental analysis found for: S 4.10, Au 64.73; atomic ratio Au/S = 2.6. HRTEM: average diameter =  $2.10 \pm 0.5$  nm. Number of gold atoms *per* core : 285. Number of ligands;  $n = 110$ . Proportion of clusterthiol = 7 %. Average number of clusterthiolate *per* particle  $n_{\text{clusterthiolate}} = 8$ ;  $n_{\text{alkylthiolate}} = 102$ . MW = 81600 g/Mol.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 4.79 (br. H, Cp); 3.40 (br. H, CHN); 1.66-1.29 (br. H alkylthiol); 0.83 (br. H,  $\text{CH}_3$  alkylthiol).  $^{13}\text{C}$  NMR (76 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 164.43 (CON); 106.91 ( $\text{C}_5\text{H}_4$ ); 99.21 ( $\text{C}_5\text{H}_5$ ); 96.14 ( $\text{C}_5\text{H}_4$ ); 31.90 ( $\text{CH}_2$  alkylthiol); 22.74 ( $\text{CH}_2$  alkylthiol); 14.31 ( $\text{CH}_3$  alkylthiol). IR (KBr,  $\text{cm}^{-1}$ ) :  $\nu_{\text{FeCO}}$  and  $\nu_{\text{CON}}$  1630.  $E_{1/2}$  (V vs.  $\text{FeCp}_2$ ;  $\text{CH}_2\text{Cl}_2$ ; 20 °C) = 0.730 (rev.); 0.045 (rev. ); -1.680 (rev.).



**Figure S1.** Titration of  $\text{H}_2\text{PO}_4^-$  with amido- $\text{Fe}_4$ -clustered AuNPs **4** in  $\text{CH}_2\text{Cl}_2$ . Decrease of the intensity of the initial CV wave (■) and increase of the intensity of the new CV wave (●) vs. the number of the equiv. of  $[\text{n-Bu}_4\text{N}][\text{H}_2\text{PO}_4]$  added *per* branch of **4** ( $3 \times 10^{-5}$  M).

## Reference

1. J. Ruiz Aranzaes, D. Astruc, *C. R. Acad. Sci. Paris*, t. 1, *Sér. IIc*, **1998**, 21; J. Ruiz Aranzaes, M.-C. Daniel, D. Astruc, *Can. J. Chem.* **2006**, 84, 288;