## **Supporting Information**

Isolation and Characterization of Tetranuclear Pt–Fe–-Fe–Pt Intermediate en Route to the Trinuclear Pt–Fe–Pt Cluster

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## Reaction of iron with Pt mononuclear complex

- An aqua solution (1 mL) containing Fe(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (18 mg, 0.05 mmol) and NaClO<sub>4</sub> (25 mg, 0.20 mmol) was slowly poured into MeOH solution (1 mL) of *cis*-[Pt(piam)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]·2H<sub>2</sub>O (23 mg, 0.05 mmol) at room temperature under the atmosphere. The color of solution change from colorless to yellow, and a yellow powder of [{PtFe(piam)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>(OCH<sub>3</sub>)}<sub>2</sub>(µ-OCH<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (1) was immediately appeared. Within several minutes, red powder of [Pt<sub>2</sub>Fe(piam)<sub>4</sub>(NH<sub>3</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub> (2) was also appeared. Using degassed solvents, similar reaction was carried out under Ar atmosphere. Mixed solution only gave a yellow powder of 1. As mentioned in text, iron oxidation state in 1 is +3, where it is unclear what is oxidizing agent.
- 2) An aqua solution (1 mL) containing Fe(ClO<sub>4</sub>)<sub>3</sub>·nH<sub>2</sub>O (18 mg, 0.05 mmol) and NaClO<sub>4</sub> (25 mg, 0.20 mmol) was slowly poured into MeOH solution (1 mL) of *cis*-[Pt(piam)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]·2H<sub>2</sub>O (23 mg, 0.05 mmol) at room temperature under the atmosphere. The color of solution change from colorless to red, and a red powder of **2** was immediately appeared.
- 3) A water suspension (1 mL) containing FeCl<sub>2</sub>·4H<sub>2</sub>O (10 mg, 0.05 mmol) and NaClO<sub>4</sub> (25 mg, 0.20 mmol) was slowly poured into MeOH solution (1 mL) of *cis*-[Pt(piam)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]·2H<sub>2</sub>O (23 mg, 0.05 mmol) at room temperature under the atmosphere. The color of solution change from colorless to yellow, and a yellow powder of 1 was immediately appeared. After 1 hour, red powder of 2 was also appeared. Compared to procedure 1), it takes much time to deposit compound 2.

## Reduction of [Pt<sub>2</sub>Fe(piam)<sub>4</sub>(NH<sub>3</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub> (2)

- A MeCN solution (10 mL) containing Fe(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (15 mg, 0.04 mmol) was slowly poured into a MeCN solution (10 mL) of *cis*-[Pt(piam)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]·2H<sub>2</sub>O (37 mg, 0.08 mmol) at room temperature under Ar. After stirring for 1 hour, a MeCN solution (100 µL) containing hydrazine monohydrate (1.0 mg, 0.02 mmol) was poured into the yellow solution, and evaporated. Resulted yellow oil was washed with CH<sub>2</sub>Cl<sub>2</sub> (2 mL) and dried for 1 hour to obtain yellow powder (36 mg) for reduced **2** of [Pt<sub>2</sub>Fe(piam)<sub>4</sub>(NH<sub>3</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>.
- 2) A MeCN solution (300 µL) containing hydrazine monohydrate (3.0 mg, 0.06 mmol) was poured into a red MeCN solution (20 mL) containing [Pt<sub>2</sub>Fe(piam)<sub>4</sub>(NH<sub>3</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub> (49 mg, 0.04 mmol) at room temperature under the atmosphere, where the color of solution immediately changed from red to light yellow. After stirring for several minutes, the light yellow solution was evaporated, washed with H<sub>2</sub>O (2 mL), and dried for 1 hour to obtain yellow powder (11 mg) for reduced 2 of [Pt<sub>2</sub>Fe(piam)<sub>4</sub>(NH<sub>3</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>.



Figure S1. IR spectra (KBr pellet) of (a)  $[{PtFe(piam)_2(NH_3)_2(OCH_3)}_2(\mu-OCH_3)_2](ClO_4)_2$  (1), (b)  $[Pt_2Fe(piam)_4(NH_3)_4](ClO_4)_3$  (2), and (c) reduced 2 of  $[Pt_2Fe(piam)_4(NH_3)_4](ClO_4)_2$ .



**Figure S2.** Molecular structure of the tetranuclear  $[{PtFe(piam)_2(NH_3)_2(OCH_3)}_2(\mu$ -OCH<sub>3</sub>)\_2]<sup>2+</sup> cation of **1** in the crystal. There are two crystallographically independent tetranuclear cations, (a) Pt(1)–Fe(1)---Fe(1')–Pt(1') and (b) Pt(2)–Fe(2)---Fe(2')–Pt(2').



Figure S3. Crystal structure of [Pt<sub>2</sub>Fe(piam)<sub>4</sub>(NH<sub>3</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub> (2) reported by W. Chen *et al.* (*Eur. J. Inorg. Chem.* 2002, 2664–2670).



Figure S4. Zero-field Mössbauer spectra of (a) 1 and (b) 2 at room temperature. Raw data are black circles, and simulated fits are red lines, and individual sites are green and blue lines. A least-squares fit of the spectrum of 1 yields an isomer shift of  $\delta = 0.32$  mm/s with no or very small quadrupole splitting (Figure S4a), which is characteristic of the high-spin Fe(+3) in 1, and this oxidation state is in agreement with both structural and XPS results. However, for 2, its broad spectrum comprises two spectra with  $\delta = -0.27$  and 1.05 mm/s with no or very small quadrupole splitting, in which isomer shifts are in the range of low-spin Fe(+2)/Fe(+3) and high-spin Fe(+2), respectively. As mentioned in the text, the results of the EPR and magnetic susceptibility measurements for 2 evidently revealed high-spin Fe(+3); this discrepancy with the Mössbauer results is difficult to interpret in the current state.



**Figure S5.** Continuous wave EPR spectra of powder samples of **1** at (a) room temperature and (b) 77 K, and **1** in (c) MeOH (2 mM) and (d) MeCN (2 mM) glass at 77 K. Experimental settings: microwave frequency, (a) 9.4485, (b) 9.0732, (c) 9.0558, and (d) 9.0679 GHz; microwave power, 6 mW; field modulation, 0.2 mT.



**Figure S6.** Continuous wave EPR spectra of **2** in (a) MeOH (2 mM) and (b) MeCN (2 mM) glass at 77 K. Experimental settings: microwave frequency, (a) 9.0527 and (b) 9.0627 GHz; microwave power, 6 mW; field modulation, 0.2 mT.



**Figure S7.** Cyclic voltammograms of 1 mM (a) **2** and (b) reduced **2** in MeCN with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte using a platinum disk working electrode, a platinum wire auxiliary electrode, and a  $Ag/Ag^+$  reference electrode (scan rate 100 mV/s). Electrode potentials were converted to those relative to Fc/Fc<sup>+</sup>.