

## **Fe<sub>3</sub>O<sub>4</sub>@organic@Au: Core-Shell Nanocomposites with High Saturation Magnetisation as Magnetoplasmonic MRI Contrast Agents**

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### **SUPPLEMENTAL INFORMATION**

**General.** Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich and used without further purification. UV-Vis data was obtained on a Cary Bio 100 UV-Vis Spectrophotometer. Data was collected over the range of 200 – 800 nm. TEM images and SAED patterns were collected on a JOEL JEM1210 at 120 kV. The diffraction patterns were compared to the reference powder diffraction files (PDF) for magnetite (# 00-019-629) and gold (# 01-089-3697). Magnetic data (ZFC/FC magnetization curves and hysteresis plots) were recorded on a commercial SQUID magnetometer (MPMS-XL - Quantum Design). The ZFC/FC curves were obtained in an applied magnetic field ( $H = 5$  mT) and performed while heating the sample in the range  $10 < T < 170$  K in zero-field-cooled (ZFC) and field-cooled (FC) procedures. Hysteresis loops were obtained at 2 K by using maximum applied fields up to 1 T in field cooling treatment.

**Relaxivity.** Longitudinal ( $T_1$ ) and transverse ( $T_2$ ) relaxation times of the nanoparticles in mQ water were measured on a Bruker Minispec mq60 NMR Analyzer at 60 MHz and 37 °C according to the inverse recovery sequence and the Carr-Purcell-Meiboom-Gill sequence, respectively. The total concentration of iron of each sample was determined by the equation below. Briefly, 5  $\mu$ L of each probe was suspended in 200  $\mu$ L HNO<sub>3</sub> and 100  $\mu$ L mQ water. Each sample was heated at 110 °C overnight, after which  $T_1$  of each solution was measured. The resulting concentration of iron was calculated from a calibration plot created from ICP-OES analysis of solutions of FeCl<sub>3</sub> in 2:1 HNO<sub>3</sub>:mQ water. For each probe, the longitudinal ( $r_1$ ) and transverse ( $r_2$ ) relaxivities were fitted to the following equation.

$$R_i [\text{Fe}] = \frac{1}{T_{i,\text{obs}}} - \frac{1}{T_{i,\text{H}_2\text{O}}}, \text{ where } i = 1, 2$$

**Fe<sub>3</sub>O<sub>4</sub>@OA.** Fe<sub>3</sub>O<sub>4</sub>@oleic acid nanoparticles were synthesized from Fe(acac)<sub>3</sub>, oleic acid, oleylamine according to a procedure developed by Wang *et al.*<sup>1</sup> Briefly, Fe(acac)<sub>3</sub> (1.4 g, 4.0 mmol), 1,2-

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<sup>1</sup> Sun, S.; Zeng, H.; Robinson, D. B.; Raoux, S.; Rice, P. M.; Wang, S. X.; Li, G. *J. Am. Chem. Soc.* **2003**, *126*, 273-279.

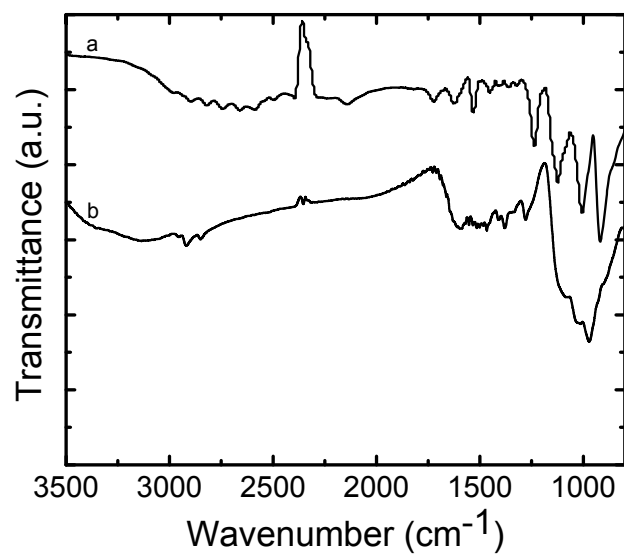
hexadecanediol (5.2 g, 20 mmol), oleic acid (3.60 mL, 12.9 mmol) and oleylamine (3.86 mL, 12.9 mmol) were dissolved in benzyl ether (40 mL) in a round bottom flask. The mixture was stirred vigorously under nitrogen and heated to for 2 hours to 200 °C followed by 1 hour at 300 °C. During this time, the mixture became black. The black suspension was then cooled to room temperature, and ethanol (80 mL) was added. The reaction mixture was centrifuged (10 min, 6000 rpm), and the black precipitate was collected. The product was re-suspended in hexanes (60 mL) with oleic acid (0.10 mL) and oleylamine (0.10 mL). The suspension was centrifuged (10 min, 6000 rpm) to remove undispersed residue. Ethanol (80 mL) was then added to precipitate the nanoparticles, which were re-suspended and stored in hexanes. The final suspension was adjusted such that a 1000-fold dilution resulted in an  $A_{350\text{ nm}} = 0.160$ . Evaporation of hexanes under ambient conditions was allowed for SQUID characterization, otherwise the sample was left as a hexanes suspension and no precipitation was evident over the course of months.

**Refunctionalization protocol -  $\text{Fe}_3\text{O}_4@$ organic.** Magnetite nanoparticles were refunctionalized with 3-aminopropylphosphonic acid according to a procedure previously reported.<sup>2</sup> A suspension of  $\text{Fe}_3\text{O}_4@$ oleic acid nanoparticles (0.5 mL) was diluted to 10 mL. A 10 mL solution of 3-aminopropylphosphonic acid (70 mg, 0.50 mmol) in water was added to a 10 mL hexanes dispersion of  $\text{Fe}_3\text{O}_4@$ OA nanoparticles, and the biphasic mixture was sonicated for 40 min. Upon completion, the layers were allowed to separate and excess water and hexanes were removed via pipet. The brown solid was washed with hexanes (3 x 1 mL) and mQ water (3 x 1 mL). The final solid was redispersed in 7 mL of mQ water such that a 10-fold dilution resulted in  $A_{350\text{ nm}} = 1.4$ . The sample was lyophilized for both IR and SQUID characterization. Otherwise, the sample was left suspended in water and no precipitation was evident over the course of weeks.

**$\text{Fe}_3\text{O}_4@$ organic@Au.**  $\text{Fe}_3\text{O}_4@$ NH<sub>2</sub> nanoparticles (0.1 mL) were diluted to 20 mL with mQ water and HAuCl<sub>3</sub> added (12.3 μL, 0.0178 mmol). The yellow solution was placed in an oil bath, sonicated for 10 min at 25 °C, and then heated to 85 °C while sonicating. At 85 °C, sodium citrate (1.25 mL, 0.25 mmol) was added and the solution was sonicated for 35 – 40 min. During this time, the reaction solution turned from yellow to clear upon addition of citrate, and then proceeded to turn dark purple, red, and finally a dark wine red. Without adjustment, the final solution was 2.22 OD/mL. The resulting colloidal solution was stable at room temperature.

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<sup>2</sup> Smolensky, E. D.; Park, H.-Y. E.; Berquo, T. S.; Pierre, V. C. *Contrast Media Mol. Imaging* in press.



**Figure S1.** Infrared spectra of a) Fe<sub>3</sub>O<sub>4</sub>@oleic acid and b) Fe<sub>3</sub>O<sub>4</sub>@organic.