Electronic Supplementary Information

Self-assembly of fluorescent and magnetic nanochains of Fe₃O₄@coordination polymer

Yoona Kim,^{‡a} Young Soo Choi,^{‡c} Hee Jung Lee,^a Hayoung Yoon,^b Young Keun Kim*^b and

Moonhyun Oh*a

^aDepartment of Chemistry, Yonsei University, 134 Shinchon-dong, Seodaemun-gu, Seoul 120-749,

Korea

^bDepartment of Material Science and Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 136-713, Korea

^cDepartment of Biomicrosystem Technology, Korea University, Seoul, Korea

*Corresponding Author ‡These authors contributed equally. Telephone number: 82-2-2123-5637 Fax number: 82-2-364-7050 Email address: moh@yonsei.ac.kr ykim97@korea.ac.kr

General Methods

Solvents and all other chemicals were obtained from commercial sources and used as received unless otherwise noted. All scanning electron microscopy (SEM) images were obtained using a JEOL-7001F field-emission SEM and energy dispersive X-ray (EDX) spectra were obtained using a Hitachi SU 1510 SEM equipped with a Horiba EMAX Energy E-250 EDS system. Transmission electron microscope (TEM) images were obtained using a JEM-2010 and a FEI Tecnai G2 F30 ST and STEM images were carried out using dark-field imaging in STEM mode at 300 kV (Korea Basic Science Institute in Seoul, Korea). EDX spectrum profile scanning was performed using a STEM attachment. All optical and fluorescence microscopy images were obtained using a Zeiss Axio Observer.D1m optical/fluorescence microscope equipped with an AxioCam MRc 5 digital camera (a filter set of 10 FITC shift free was used for green emission). Magnetic properties of Fe₃O₄@CP nanochains were measured using a vibrating sample magnetometer (EV9-380 V, MicroSense). The Fourier transform infrared spectra (FTIR) of solid samples were obtained with a Jasco FT-IR 4200 LE spectrometer using a KBr pellet. Emission spectra were obtained on a Jasco FP-8500 fluorometer using quartz cells (10 x 4 mm light path).

Preparation of PAA-functionalized Fe₃O₄ nanoclusters

Magnetite (Fe₃O₄) nanoclusters with two different sizes were synthesized by a hydrothermal polyol process.¹ FeCl₃· $6H_2O$ (0.8109 g, 3 mmol), NaOAc (0.9844 g, 12 mmol) and distilled water (2.7 mL, 150 mmol) were dissolved in ethylene glycol (50 mL) with a vigorous mechanical stirring. Under steady stirring, the resulting solution was refluxed for 8 hrs. Fe₃O₄ nanoclusters (160 nm) generated in this time were isolated using a permanent magnet and were washed with absolute ethanol and distilled water several times. Fe₃O₄ nanoclusters (270 nm) were also prepared from a similar hydrothermal polyol process using FeCl₃· $6H_2O$ (0.8109 g, 3 mmol), NaOAc (0.7383 g, 9 mmol) and distilled water (2.7 mL, 150 mmol). Poly acrylic acid (PAA) functionalized Fe₃O₄ nanoclusters

were then prepared by reaction of Fe_3O_4 nanoclusters (10 mg) and PAA (0.5 g) in 10 mL distilled water at RT for 6 hrs.² The resulting products were washed several times with distilled water.

Preparation of $Fe_3O_4(a)CP$ nanochains

A precursor solution of coordination polymer was prepared by mixing $In(NO_3)_3$ (1 mg, 2.56 µmol) and *N,N'*-phenylenebis(salicylideneimine)dicarboxylic acid (H₂L, 1 mg, 2.47 µmol). The PAAfunctionalized magnetite (Fe₃O₄) nanoclusters (0.05 mg) were then added to the resulting precursor solution. The mixture was immersed in an oil bath and heated on a magnetic hot plate (Corning PC-420D, 140 °C) without rotation. Nanochains of Fe₃O₄@CP generated within 20 min were isolated using a magnetic bar and were washed several times with fresh DMF and acetonitrile. The resulting Fe₃O₄@CP was characterized by SEM, TEM, FM, EDX spectroscopy and IR spectroscopy. FTIR (KBr pellet, cm⁻¹) : 1611s, 1582s, 1512m, 1476m, 1423w, 1380s, 1308m, 1284m, 1249m, 1184m, 1130w, 976w, 957w, 874w, 850w, 791m, 748w, 702m, 637m, 593w. Irregularly aggregated Fe₃O₄@CP was prepared *via* a similar solvothermal reaction heated using a hot plate without a magnetic stirring function (Corning PC-400D) under otherwise identical reaction conditions to those described above.

Coordination polymer shell thickness control of Fe₃O₄@CP

The thickness of the coordination polymer shell within Fe₃O₄@CP nanochains was controlled by varying the amounts of coordination polymer precursors used in the reactions (H₂L; 0.5~2 mg, In(NO₃)₃; 0.5~2 mg) under otherwise identical reaction conditions to those described above. The same amount of Fe₃O₄ nanoclusters (0.05 mg) was used in all reactions.

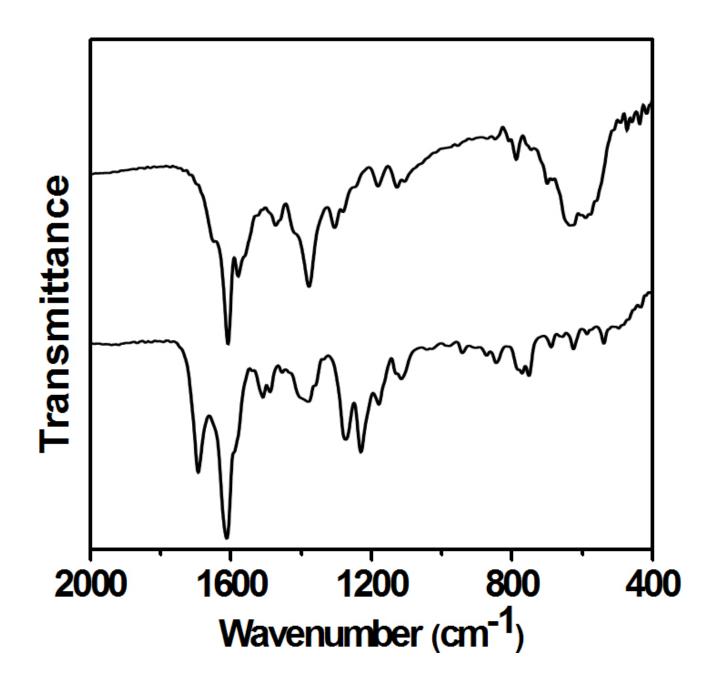


Fig. S1 IR spectra of organic building blocks H₂L (bottom) and Fe₃O₄@CP nanochains (top).

References

1 J. Cha, J. S. Lee, S. J. Yoon, Y. K. Kim and J.-K. Lee, *RSC Adv.*, 2013, **3**, 3631-3637.

2 Y.-H. Ma, S.-Y. Wu, T. Wu, Y.-J. Chang, M.-Y. Hua and J.-P. Chen, *Biomaterials*, 2009, **30**, 3343-3351.