Supporting Information

Orientation-Selective Alignments of Nanoblocks in *a* and *c* Directions of a Tetragonal System through Molecularly Mediated Manipulation

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Experimental procedures

Synthesis and characterization of Mn_3O_4 rectangular nanoblocks

In 31 cm^3 of water in a 100 cm^3 Teflon container, 0.60 mmol manganese(II) chloride and 35wt% hydrogen peroxide (4 cm^3) were dissolved. Oleic acid (3.97 mmol) and *tert*-butylamine (2.31 mmol) were added to 30 cm^3 of toluene. The organic mixture was added to the Teflon container without stirring. At this time, oxygen gas was generated through the decomposition of hydrogen peroxide. When the generation of oxygen gas roughly stopped, the Teflon container was placed into a stainless steel autoclave. The autoclave was heated at 115°C for 12 h. After the reaction, the resultant dark brown liquid (the upper phase) was transferred into a glass vial. A copper grid covered with a collodion film was placed on a piece of filter paper. A drop of the resultant dispersion was placed on the grid. The excess medium of the dispersion was absorbed by the filter paper. The products deposited on the grid were characterized using transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and fast Fourier transform (FFT) profiles. Exchange of adsorbed molecules on surfaces of Mn_3O_4 rectangular nanoblocks

Exchange of adsorbed molecules on surfaces of Mn_3O_4 rectangular nanoblocks

The resultant dispersion of Mn_3O_4 nanoblocks was centrifuged at 13500 rpm for 5 min. The volume of the dispersions was 1 cm^3. The precipitates were redispersed into 10 cm^3 of pure water containing hexamethylenediamine (11 mg). The liquid was treated by ultrasonication (Branson, Sonifier 450, output control 1) for 30 min. After ultrasonication, water was evaporated using a vacuum dryer at 80˚C. The resultant precipitates were redispersed into a hexane–toluene mixture (1 : 1 in volume, 1 cm^3).