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Magnetic nanoparticle-supported crown ethers

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General Remarks

Reagents were purchased from Tokyo Kasei Kogyo, Kanto Chemical, Aldrich and Wako Pure Chemical Industries, and used as received unless otherwise noted. Hexane and toluene were distilled from CaH_2 prior to use. ^1H and ^{13}C NMR were recorded on a JEOL JMN-LA500 (499 MHz for ^1H, 125 MHz for ^{13}C) using $CDCl_3$ as a solvent, and tetramethylsilane as an internal standard. Potassium acetate and potassium iodide were ground to powder using a mortar and pestle, and then dried under reduced pressure prior to use. GC analyses were performed on a Shimadzu GC-17A using an UA^+-1 capillary column (30 M × 0.25 mm, FRONTIER LABORATORIES). FAB-MS was measured on a JEOL MS600H spectrometer using glycerol as matrix. Scanning electron microscopy (SEM) was performed on a TOPCON DS-720 Scanning Electron Microscope using conventional sample preparation and techniques. Transmission electron microscopy (TEM) was carried out on a Hitachi H-9000NA operating at 300 kV. Magnetite nanoparticles[1] and **1**[2] were synthesized according to the literature method.

Preparation of 2

(3-Isocyanato)propyltriethoxysilane (1.13g, 4.57 mmol) was added to a solution of 4′-aminobenzo-18-crown-6 (1.36 g, 4.15 mmol) in toluene (10 ml). The mixture was stirred for 12 h at 85 °C. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure. The obtained yellow viscous oil was washed with hexane five times and dried *in vacuo* to give 2.19 g (92% yield) of **2** as a pale yellow solid.

^{1}H NMR (499 MHz, $CDCl_3$): $\delta = 0.59$-0.65 (m, 2H), 1.21 (t, 9H, $J = 7.0$ Hz), 1.57-1.65 (m, 2H), 3.21 (q, $J = 6.7$ Hz, 2H), 3.67-3.84 (m, 18H), 3.88-3.92 (m, 4H), 4.08-4.14 (m, 4H), 5.11 (br t, $J = 5.8$ Hz, 1H), 6.55 (br s, 1H), 6.69 (dd, 1H, $J = 2.3$, 8.6 Hz), 6.78 (d, 1H, $J = 8.6$ Hz), 7.02 (d, 1H, $J = 2.3$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 7.66$, 18.31, 23.59, 42.75, 58.45, 69.02, 69.62, 69.74, 69.78, 70.77, 70.80, 70.82, 70.87, 70.89, 109.25, 114.74, 115.23, 132.57, 145.79, 149.58, 156.32. MS (FAB+, glycerol) *m*/*z* 575 ($[M+H]^+$). Anal. Calc. for $C_{26}H_{46}N_2O_{10}Si$: C, 54.33; H, 8.07; N, 4.87. Found: C, 54.34; H, 8.01; N, 4.83.

General procedure for preparation of the MNP-supported crown ethers

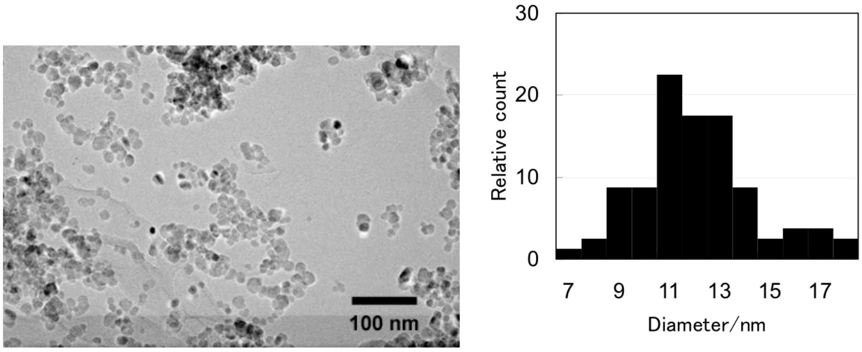
A mixture of magnetite nanoparticles (741 mg, 3.20 mmol, average diameter = 12 nm), **2** (426 mg, 0.741 mmol), H_2O (65 μl), and EtOH (10 ml) was ultra-sonicated for 1 min and then stirred at refluxing temperature for 12 h. After cooling to room temperature, the particles were separated by magnetic decantation using an external magnet and washed five times with EtOH. After drying under reduced pressure, 723 mg of **4** was obtained as a dark brown powder. The catalyst loading was determined to be 0.249 mmol/g by elemental microanalysis of nitrogen.

General procedure for halogen exchange reaction of *n*-C_8H_{17}Br

In a 5 ml sealed tube with a Teflon plug, a mixture of the catalyst (0.0225 mmol), KI (623 mg, 3.75 mmol), 1-bromooctane (130 μl, 0.75 mmol), toluene (1 ml), and *n*-tetradecane (20 μl) was stirred at 100 °C for 8 h. After cooling to room temperature, yield was determined by GC using *n*-tetradecane as an internal standard.

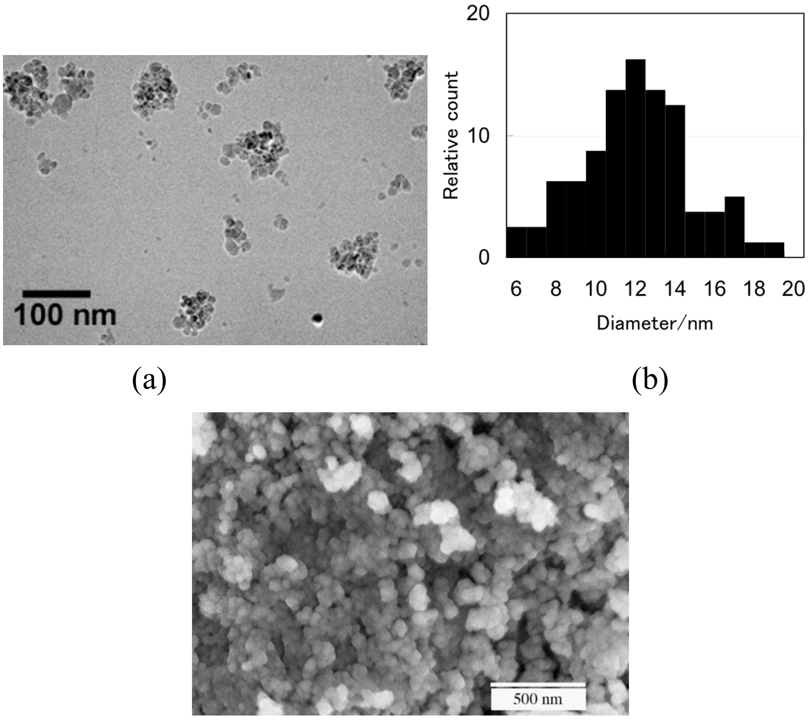
General procedure for substitution reaction of BnBr with AcOK and catalyst reuse

In a 5 ml sealed tube with a Teflon plug, a mixture of catalyst (0.0225 mmol), potassium acetate (221 mg, 2.25 mmol), benzyl bromide (89 μl, 0.75 mmol), toluene (1 ml), and *n*-tetradecane (20 μl) was stirred at 80 °C for 8 h in a sealed glass tube. After the reaction, yield was determined by GC using *n*-tetradecane as an internal standard. The catalyst was concentrated on the sidewall of the reaction vessel using an external magnet, and the organic phases were separated. The residual catalyst was washed five times with hexane, H_2O and EtOH, respectively. Finally, the catalyst was washed twice with hexane and then dried under reduced pressure. The obtained catalyst in the reaction vessel was subjected to the next run without any treatment.



(a) (b)

Fig. S-1 (a) TEM image of non-coated Fe_3O_4. (b) Particle size distribution measured from TEM images of non-coated Fe_3O_4. The average diameter was calculated to be 12 nm.



(a) (b)

(c)

Fig. S-2 (a) TEM image of **4**. (b) Particle size distribution measured from TEM images of **4**. The average diameter was calculated to be 12 nm. (c) SEM image of **4**.

References

1. Liu, X.; Ma, Z.; Xing, J.; Liu, H. *J. Magn. Magn. Mater.* **2004**, *270*, 1-6.

2. Barboiu, M.; Cerneaux, S.; van der Lee, A.; Vaughan, G. *J. Am. Chem. Soc.* **2004**, *126*, 3545-3550.