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SUPPORTING INFORMATION

Clickable Complexing Agents: Functional Crown Ethers for Immobilisation Onto Polymers and Magnetic Nanoparticles

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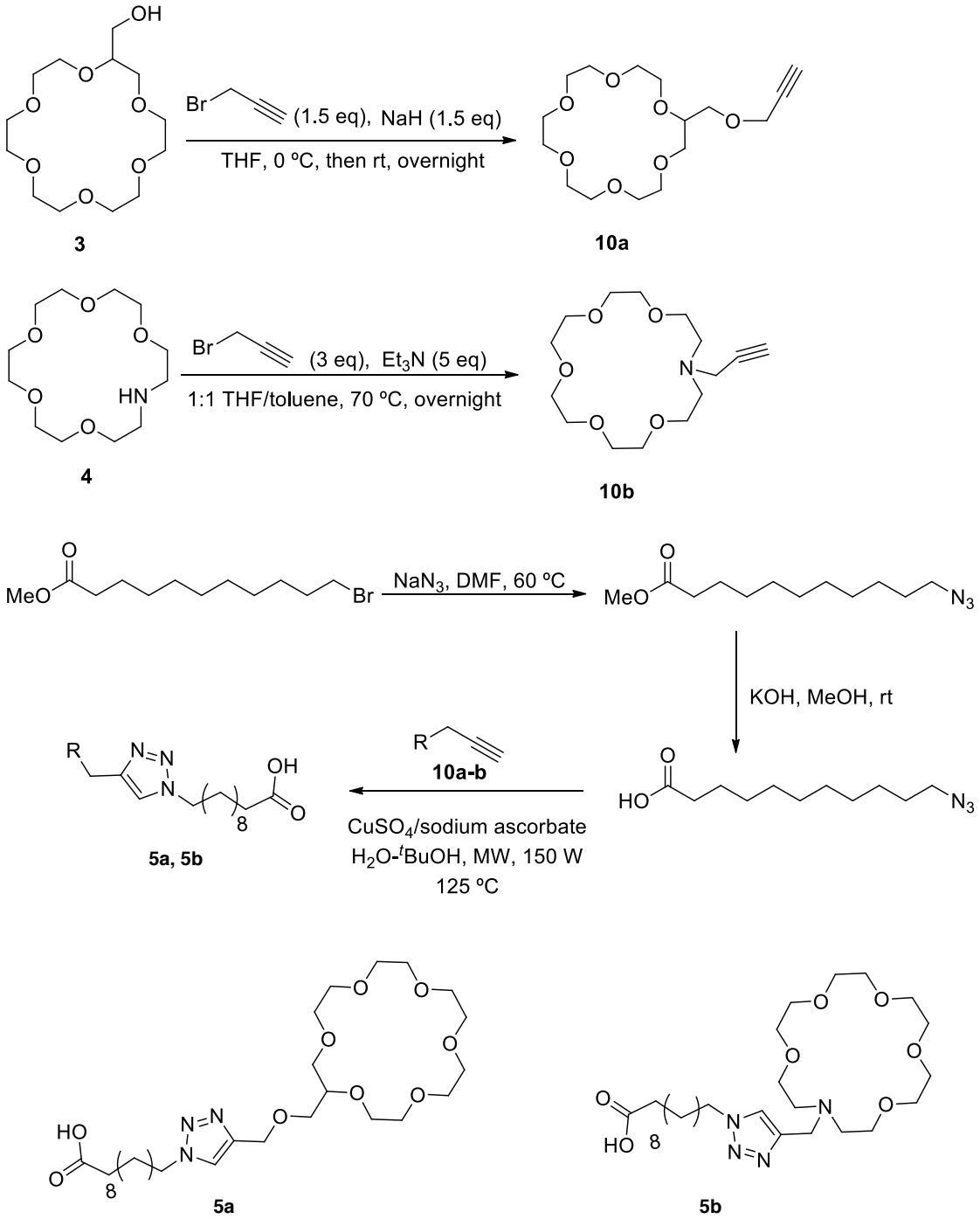
1 GENERAL

Unless otherwise stated, all commercial compounds were used as received without any further purification. Ultra pure water was obtained from an SG Water Ultra clear basic system, that provides water with a conductivity at 25 ºC of 0.055 μS. Dry solvents (CH_2Cl_2, THF, DMF, diethyl ether, hexane and toluene) were obtained from a Puresolv^{TM} purification system that removes water and oxygen. Dry *o*-dichlorobenzene, methanol, *n*-pentane and xylene were obtained by treatment with pellets of 4 Å molecular sieves (previously activated by microwave irradiation) under argon atmosphere. When degassed solvents were required, an argon stream was passed through the solvent. NMR spectra were recorded on a Bruker Avance 400 Ultrashield NMR spectrometer or in a Bruker Avance 500 Ultrashield NMR spectrometer at room temperature unless otherwise stated. For ^{1}H NMR all chemical shifts are reported in ppm relative to the proton resonance resulting from incomplete deuteration of the corresponding NMR solvent: CD_3OD (3.31 ppm), $CDCl_3$ (7.27 ppm) and CD_2Cl_2 (5.32 ppm). For ^{31}P NMR spectra all chemical shifts are reported in ppm relative to external 85% H_3PO_4. In the case of ^{13}C NMR spectra all chemical shifts are reported in ppm relative to the carbon resonance of the corresponding deuterated NMR solvent: CD_3OD (49.15 ppm), CD_2Cl_2 (54 ppm) and $CDCl_3$ (77.23 ppm). ^{1}H and ^{13}C experiments of polymers were performed with a Bruker Avance spectrometer operating at a frequency of 500.13 MHz using a Bruker 4 mm $^{1}H/^{13}C/^{2}H$ gradient HR-MAS probe. *J* values are given in Hz. IR spectra were recorded on a Bruker Tensor 27 FTIR spectrometer fitted with an ATR cell. IR spectra of nanoparticles were recorded on a Bruker Tensor 27 FTIR spectrophotometer or in a Thermo Nicolet 5700 FTIR spectrometer, using KBr pellets. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-1011 transmission electron microscope equipped with a lanthanum hexaboride filament operated at an acceleration voltage of 100 kV. Reactions heated under microwave irradiation were performed in a CEM Discover microwave synthesis apparatus using 10 mL vessels with septa for reactions performed at elevated temperatures and pressures. Thermogravimetric analyses were performed in a Mettler Toledo TGA/SDTA 851^{e} thermo balance. TGA results in the product description were recorded under nitrogen stream (80 mL/min) and with a heating rate of 10 ºC/min.

2 PREPARATION AND FUNCTIONALISATION OF COBALT NANOPARTICLES

2.1 Preparation of carboxylic acids 5a-b



2-((Prop-2-ynyloxy)methyl)-1,4,7,10,13,16-hexaoxacyclooctadecane (10a)

Sodium hydride (60% dispersion in mineral oil) (0.048 g, 1.19 mmol) was placed in a 25 mL Schlenk flask and washed under argon atmosphere with 3 portions of 2 mL of anhydrous hexane. Then 2.5 mL of anhydrous THF were added and the mixture was cooled to 0 ºC in an ice bath. When this temperature was reached a solution of 2-(hydroxymethyl)-18-crown-6 (≥ 90%) (0.259 g, 0.791 mmol) in anhydrous THF (3 mL) was added *via* cannula. The reaction mixture was stirred at 0 ºC for 2 h. After this time propargyl bromide 80% in toluene (0.128 mL, 1.19 mmol) was added with a syringe. The reaction mixture was slowly warmed-up to room temperature and stirred overnight at room temperature. Subsequently, the reaction was carefully quenched with water (14 mL), and the mixture was extracted with 3 × 14 mL of CH_2Cl_2. The combined organic extracts were washed with 3 × 20 mL water, dried over anhydrous magnesium sulphate and filtered. The solvent was removed under reduced pressure. The yellow residue was purified by flash column chromatography on alumina (eluting with hexane/ethyl acetate 20:80 and hexane/ethyl acetate 5:95) to yield **10a** (0.228 g, 87% yield) as a colourless oil. ν_{max}/cm^{-1} 3245, 2867, 2113, 1719, 1451,1350, 1250, 1098, 946, 847; δ_H (400 MHz, $CDCl_3$) 4.19 (2 H, d, $^4J_{H\text{-}H}$ 2.36, C*H*$_2$CCH), 3.83 (2 H, m, O-C*H*$_2$), 3.78 (1 H, m, -OCH$_2$C*H*O), 3.58-3.75 (22 H, m, methylenic H from crown ether), 2.42 (1 H, t, $^4J_{H\text{-}H}$ 2.36, -CC*H*-); δ_C (100.6 MHz, $CDCl_3$) 79.94 (*C*CH), 78.44 (O*C*HCH$_2$), 74.67 (*C*HC), 71.77(*C*H$_2$O), 71.14, 71.11, 71.05, 70.96, 70.9, 70.2, 70.1, 70.08, 58.8 (O*C*H$_2$CCH); *m/z* (TOF MS ES+) calculated for $C_{16}H_{28}O_7Na^+$ (M+Na) 355.1727, found 355.1729

16-(Prop-2-ynyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (10b)

1-Aza-18-crown-6 (95%) (0.212 g, 0.765 mmol) was dissolved in 14 mL of a 1:1 mixture of anhydrous THF and anhydrous toluene, in a Schlenk flask. Triethylamine 99.5% (0.391 g, 0.540 mL, 3.83 mmol) was added and the mixture was heated (60 ºC) for about 15 minutes. Propargyl bromide solution (80% in toluene) (0.247 mL, 2.296 mmol) was added and the mixture was heated overnight at 70 ºC, with stirring. After cooling to room temperature, the white precipitate that was present was separated by filtration, washed with 2 × 4 mL of anhydrous THF and the filtrate, together with the washings, were evaporated to dryness. The residue suspended in 40 mL water and extracted two times with CH_2Cl_2 (40 mL each). The organic fraction was again washed

with 20 mL water, dried with anhydrous $MgSO_4$ and evaporated to dryness to render **10b** (0.218 g, 94% yield) as a yellow oil, that was used without any further purification. Found: C, 60.88; H, 9.42; N, 4.07%. Calc for $C_{15}H_{27}NO_5$: C, 59.78; H, 9.03; N, 4.65%. ν_{max}/cm^{-1} 3242, 2961, 2921, 2854, 2107, 1608, 1450, 1352, 1260, 1095, 1018, 947, 863, 797, 661; δ_H (400 MHz, $CDCl_3$) 3.62-3.74 (20 H, m, various methylenic H from the crown ether), 3.52 (2 H, d, $^4J_{H\text{-}H}$ 2.3, CH_2CCH), 2.84 (4 H, t, $^3J_{H\text{-}H}$ 5.6, -NCH_2-CH_2), 2.18 (1 H, t, $^4J_{H\text{-}H}$ 2.3, -CC*H*); δ_C (100.6 MHz, $CDCl_3$) 79.44 (-*C*CH), 72.93 (-C*C*H), 70.97 (*C*H_2), 70.95 (*C*H_2), 70.55 (*C*H_2), 69.73 (*C*H_2), 53.4 (-N*C*H_2-CH_2), 43.9 (*C*H_2CCH); *m/z* (TOF MS ES+) calculated for $C_{15}H_{28}NO_5^+$ ($M+H^+$) 302.1962, found 302.1958.

Methyl 11-azidoundecanoate

This compound was prepared following a previously reported procedure.[1] Sodium azide 99.5 % (44.5 mg, 0.7 mmol) was placed in a 25 ml round-bottomed flask connected to a Dimroth condenser, and dissolved under argon atmosphere in 10 mL of anhydrous DMF. To this solution, 0.17 mL (0.67 mmol) of methyl 11-bromoundecanoate (95 %) were added, and the mixture was heated at 60 ºC for 3 days. After cooling to room temperature, the reaction mixture was poured over 100 mL of water and extracted with 3 portions of 100 mL of diethyl ether. The combined organic extracts were washed with 2 portions of 50 mL of cool water first, and then with 40 mL of brine. The organic layer was dried over anhydrous magnesium sulphate, filtered, and purified by flash chromatography on silica gel (90:10 hexane/diethyl ether). Evaporation of the solvent rendered the methyl ester product (0.146 g, 89 % yield) as a translucent oil. ^{1}H NMR matched the reported data.[1] δ_H (400 MHz, $CDCl_3$) 3.67 (3 H, s, CH_3), 3.25 (2 H, t, $^3J_{H\text{-}H}$ 7.0), 2.30 (2 H, t, $^3J_{H\text{-}H}$ 7.6), 1.68-1.54 (4 H, m), 1.40-1.22 (12 H, m).

11-Azidoundecanoic acid

Methyl 11-azidoundecanoate (2.47 g, 10.23 mmol) was dissolved in methanol (20 mL) and a solution of KOH (5.41 g, 82 mmol) in 50 mL of methanol was added. The solution turned immediately yellow. The reaction mixture was stirred overnight at room temperature. After this time, methanol was removed under reduced pressure and the colourless residue was dissolved in water (100 mL). After washing with ethyl acetate,

the aqueous phase was acidified with 1 N HCl (140 mL) and extracted with ethyl acetate (3 × 150 mL). The combined organic layers were dried over magnesium sulphate, filtered and evaporated to render 11-azidoundecanoic acid (2.23 g, 96%) as a light yellow oil. All the spectroscopic data matched with those reported in the literature.[2] ν_{max}/cm^{-1} 2952, 2841, 2675, 2091 (s, N_3), 1705 (s, C=O), 1458, 1411, 1348, 1283 (m), 1253 (m), 1104, 1054, 932, 722, 665, 625; δ_H (400 MHz, $CDCl_3$) 3.25 (2 H, t, $^3J_{H\text{-}H}$ 7.0), 2.34 (2 H, t, $^3J_{H\text{-}H}$ 7.5), 1.7-1.5 (4 H, m), 1.42-1.20 (12 H, m). δ_C (100 MHz, $CDCl_3$) 180.6 (C), 51.6 (CH_2), 34.3 (CH_2), 29.6 (CH_2) (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 26.9 (CH_2), 24.8 (CH_2).

11-(4-((1,4,7,10,13,16-Hexaoxacyclooctadecan-2-ylmethoxy)-methyl)-1H-1,2,3-triazol-1-yl)undecanoic acid (5a)

Compound **10a** (100 mg, 0.30 mmol), together with 11-azidoundecanoic acid (68 mg, 0.30 mmol), L-ascorbic acid sodium salt (99%) (30 mg, 0.150 mmol), and copper (II) sulphate pentahydrate (3.8 mg, 0.015 mmol) were placed in a microwave tube, and dissolved in 2 mL of a 1:1 mixture of water/ *tert*-butyl alcohol. The mixture was stirred under microwave irradiation at 125 ºC and 150 W for 20 min. Then 6 mL of water were added, and the mixture was extracted with 3 × 10 mL of ethyl acetate. The combined organic extracts were washed with 15 mL water, dried over anhydrous magnesium sulphate, filtered and evaporated to dryness to yield **5a** (0.122 g, 73%) as yellow oil. ν_{max}/cm^{-1} 3133, 2922, 2855, 1724 (C=O), 1463, 1351, 1295.6, 1249, 1222, 1107, 1049, 990, 946, 630; δ_H (400 MHz, $CDCl_3$) 7.55 (1 H, s, C=C*H*-N), 4.66 (2 H, m, N-N-CH_2), 4.34 (2 H, t, $^3J_{H\text{-}H}$ 7.1, CH_2N), 3.80 (2 H, m, OCH_2-CH), 3.59-3.78 (23 H, m), 2.34 (2 H, t, $^3J_{H\text{-}H}$ 7.4, CH_2COOH), 1.90 (2 H, m, CH_2CH_2N), 1.63 (2 H, m, CH_2CH_2COOH), 1.30 (12 H, m); δ_C (100 MHz, $CDCl_3$) 177.6 (-*C*OOH), 145.5 (CH_2-*C*=CH), 122.5 (C=*C*H), 78.6 (O*C*HCH_2), 71.8 (O-CH-*C*H_2), 71.1, 71.05, 71.0, 70.95, 70.9, 70.9, 70.2, 70.1, 65.2 (*C*H_2-C=CH), 50.6 (N-*C*H_2), 34.1 (*C*H_2COOH), 30.4, 29.3, 29.2, 29.1, 29.0, 26.6, 24.9; *m/z* (TOF MS ES+) calculated for $C_{27}H_{49}N_3O_9Na^+$ ($M+Na^+$) 582.3361, found 582.3328.

11-(4-((1,4,7,10,13-Pentaoxa-16-azacyclooctadecan-16-yl)methyl)-1H-1,2,3-triazol-1-yl)undecanoic acid (5b)

Compound **10b** (100 mg, 0.332 mmol), 11-azidoundecanoic acid (75.4 mg, 0.332 mmol), L-ascorbic acid sodium salt (99%) (33.2 mg, 0.166 mmol), and copper (II) sulphate pentahydrate (4.2 mg, 0.017 mmol) of were placed in a microwave tube, and dissolved in 2 mL of a 1:1 mixture of water/ *tert*-butyl alcohol. The mixture was heated under microwave irradiation, at 125 ºC and 150 W for 60 minutes. Then 4 mL of water were added, pH was checked using pH indicator paper and the mixture was acidified if needed. The mixture was extracted once with ethyl acetate (5 mL). The aqueous layer was then neutralised and extracted with 3 × 10 mL of CH_2Cl_2. The combined CH_2Cl_2 extracts were dried over anhydrous magnesium sulphate, filtered and evaporated to dryness to yield product **5b** (129 mg, 72% yield) as a pale yellow oil. ν_{max}/cm^{-1} 3132, 2922, 2854, 1717 (C=O), 1541, 1457, 1351, 1295.1, 1248, 1216, 1111, 1048, 989, 946, 835, 721; δ_H (400 MHz, $CDCl_3$) 7.75 (1 H, s, C=C*H*-N), 4.36 (2 H, t, $^3J_{H\text{-}H}$ 6.9, N-N-CH_2), 4.03 (2 H, s, HC=CCH_2), 3.48-3.83 (22 H, m), 2.94 (4 H, br s, OCH$_2$CH_2N), 2.35 (2 H, br s, CH_2COOH), 1.91 (2 H, br m, CH_2CH$_2$N-N), 1.63 (2 H, br, CH_2CH$_2$COOH), 1.30 (12 H, m); δ_C (100 MHz, $CDCl_3$) 124.0 (C=*C*H), 70.8, 70.7, 70.6, 68.5, 53.2, 50.3 (N-*C*H$_2$), 30.1, 28.9, 28.8, 28.7, 28.6, 28.4, 26.1; δ_H (500 MHz, toluene-*d8*, 378K) 7.30 (1 H, s, C=CH-N), 3.94 (2 H, t, $^3J_{H\text{-}H}$ 7.1, NN-CH_2), 3.92 (2 H, s, C=CCH_2), 3.58 (4 H, t, $^3J_{H\text{-}H}$ 5.6, OCH_2CH$_2$-N crown), 3.45-3.56 (16 H, m), 2.84 (4 H, t, $^3J_{H\text{-}H}$ 5.0, OCH$_2$CH_2N crown), 2.16 (2 H, t, $^3J_{H\text{-}H}$ 7.2, CH_2COOH), 1.66 (2 H, m, CH_2CH$_2$N-N), 1.57 (2 H, m, CH_2CH$_2$COOH), 1.32 – 1.10 (12 H, m); δ_C (500 MHz, toluene-*d8*, 378K) 172.98, 145.4, 122.6 (C=*C*H), 70.7, 71.5, 71.2, 70.7, 55.25, 51.49, 50.03, 34.0, 30.47, 29.34, 29.32, 29.3, 29.0, 26.8, 25.5; *m/z* (TOF MS ES+) calculated for $C_{26}H_{49}N_4O_7^+$ ($M+H^+$) 529.3596, found 529.3613

2.2 Preparation of functional cobalt nanoparticles 6a-b

The following procedure describes the preparation of nanoparticles **6b**. The preparation of the analogous particles **6a**, involving crown ether derivative **5a**, is described in the main text.

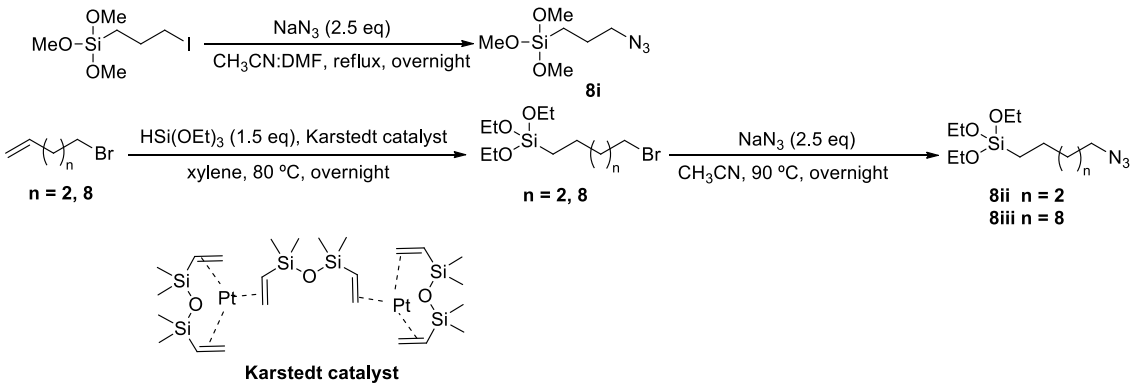
Cobalt nanoparticles functionalised with crown ether derivative 5b: preparation of nanoparticles 6b

Azacrown ether derivative **5b** (117 mg, 0.221 mmol) and TOPO >97% (17.6 mg, 0.0442 mmol) were weighed in a 25 mL two-necked round-bottomed flask and

dissolved under an argon atmosphere in 2.4 mL of anhydrous and degassed *o*-dichlorobenzene. To this suspension, 36 μL of oleic acid (31.8 g, 0.1103 mmol) were injected and the mixture was heated in a silicone oil bath at 160 ºC, with mechanical stirring using a shaker. When the bath had reached the desired temperature, a solution of 84 mg (0.2211 mmol) of $[Co_2(CO)_8]$ (≥ 90 %) in 3 mL of anhydrous, degassed, *o*-dichlorobenzene was rapidly transferred into the reaction media by injection. The reaction mixture was mechanically stirred at 160 ºC for 1 hour. After cooling to room temperature, 9 mL of anhydrous and degassed methanol were added. The resulting suspension was stored in the freezer under argon until the precipitation of the particles (1.5 hours). The particles were separated by magnetic decantation and washed once with anhydrous, degassed methanol (20 mL) and with anhydrous, degassed dichloromethane (60 mL). The solvents were removed *in vacuo* and the residual solid was dried under a nitrogen stream. In this manner, 12.3 mg of cobalt nanoparticles were obtained with a particle size of 9.04 nm (s = 2.81). According to the %N determined by elemental analysis a functionalisation of the nanoparticles of f = 0.113 mmol/g was obtained. Elemental analysis found: C, 9.42; H, 1.63; N, 0.63. ν_{max}/cm^{-1} 3449, 2920, 2851, 1466, 1404, 1110, 833. TGA (30 – 900 ºC, 10 ºC/min, under N_2; for a 3.5660 mg sample, % weight loss): 4.9790 (onset: 137.34 ºC), 17.8415 (onset: 281.50 ºC), 8.0653 (left limit: 345.11 ºC, right limit: 646.38 ºC).

3 PREPARATION AND FUNCTIONALISATION OF MAGNETITE NANOPARTICLES

3.1 Preparation of alkoxysilanes 8i-8iii



3-Azidopropyltrimethoxysilane (8i)

This compound was prepared by slight modifications of a previously reported procedure[3]. Sodium azide 95.5% (4.13 g, 60.7 mmol) was suspended in a mixture of anhydrous acetonitrile (80 mL) and 2 mL DMF, under argon in a Schlenk flask. To this mixture 3-iodopropyltrimethoxysilane 95% (5 mL, 24.3 mmol) was added with a syringe under stirring. The resulting white suspension was then stirred overnight at reflux. The reaction mixture was allowed to cool down to room temperature, the solvent was evaporated under reduced presure, dry pentane (45 mL) was added and the reaction mixture was stirred for 15 minutes. The pentane layer was transferred to another Schlenk flask using a cannula fitted with filter paper, a second addition of dry pentane was done and the process was repeated. The solvent was evaporated under reduced pressure to yield **8i** as clear yellow liquid (4.24 g, 85% yield). All the spectroscopic data matched with those reported in the literature.[3] ν_{max}/cm^{-1} 2942, 2841, 2094 (N_3), 1457, 1413, 1344, 1275, 1241, 1189, 1079, 883, 816, 628; δ_H (400 MHz, $CDCl_3$) 3.58 (9 H, s, CH_3), 3.27 (2 H, t, $^3J_{H\text{-}H}$ 6.9), 1.77 – 1.67 (2 H, m), 0.75 – 0.66 (2 H, m); δ_C (100 MHz, $CDCl_3$) 53.9 (CH_2), 50.7 (CH_3), 22.7 (CH_2), 6.5 (CH_2).

5-Bromopentyltriethoxysilane

This compound was prepared following a previously reported procedure.[4] 5-bromo-1-pentene 95% (0.4 mL, 3.19 mmol) was placed in a Schlenk flask under an argon atmosphere and was dissolved in 0.5 mL of anhydrous xylene. Triethoxysilane 95% (0.92 mL, 4.78 mmol) and Karstedt catalyst solution in xylene (2% in platinum) (1.82 mL, 0.16 mmol) were mixed together in another Schlenk flask and the mixture was added to the 5-bromo-1-pentene solution *via* cannula. The reaction mixture was stirred overnight at 80 ºC. After cooling to room temperature the solution was filtered through Celite to separate the metal residues. The solvent was removed under vacuum and the crude product was used in the next step without any further purification. All the spectroscopic data matched with those reported in the literature.[4] ν_{max}/cm^{-1} 2976, 2929, 2891, 1166, 1102, 1078, 957; δ_H (400 MHz, $CDCl_3$) 3.82 (6 H, q, $^3J_{H-H}$ 7.0, OCH_2), 3.41 (2 H, t, $^3J_{H-H}$ 6.9, CH_2Br), 1.93 – 1.81 (2 H, m, CH_2CH_2Br), 1.52 – 1.38 (4 H, m, -CH_2CH_2-), 1.23 (9 H, t, $^3J_{H-H}$ 7.0, CH_3), 0.68 – 0.61 (2 H, m, -SiCH_2-); δ_C (100.6 MHz, $CDCl_3$) 58.6, (O*C*H_2CH$_3$), 34.1 (*C*H_2Br), 32.7, 31.8, 22.3 (3 *C*H_2), 18.5 (*C*H_3), 10.54 (Si*C*H_2);

5-Azidopentyltriethoxysilane (8ii)

This compound was prepared following a previously reported procedure.[4] 5-bromopentyltriethoxysilane (0.52 g) was transferred to a 25 mL Schlenk flask and 7 mL of dry acetonitrile were added. Sodium azide 95.5% (0.27 g, 4.16 mmol) was added to the reaction medium as a solid. The reaction mixture was stirred at 90 ºC for 48 hours. The solvent was evaporated, 20 mL dry pentane was added and the suspension was filtered. The solvent of the resulting filtrate was removed *in vacuo* and **8ii** (0.39 g, 44% yield for the two combined steps) was obtained as a yellow oil and used without any further purification. All the spectroscopic data matched with those reported in the literature.[4] ν_{max}/cm^{-1} 2972, 2927, 2885, 2099 (N_3), 1444, 1391, 1260, 1167, 1102, 1080, 958, 797; δ_H (400 MHz, $CDCl_3$) 3.82 (6 H, q, $^3J_{H-H}$ 7.0, -CH_2-O-), 3.26 (2 H, t, $^3J_{H-H}$ 7.0, CH_2N$_3$), 1.61 (2 H, m, CH_2CH_2N$_3$), 1.43 (4 H, m, - CH_2CH_2-), 1.24 (9 H, t, $^3J_{H-H}$ 7.0, CH_3), 0.65 (2 H, m, SiCH_2); δ_C (100.6 MHz, $CDCl_3$) 58.61 (*C*H_2CH$_3$) 51.67 (*C*H_2N$_3$), 30.36 (3 *C*H_2), 28.76, 22.71, 18.56 (*C*H_3), 10.61 (Si*C*H_2); *m/z* (ESI+) 298.1 ($[M+Na]^+$, 13.5%)

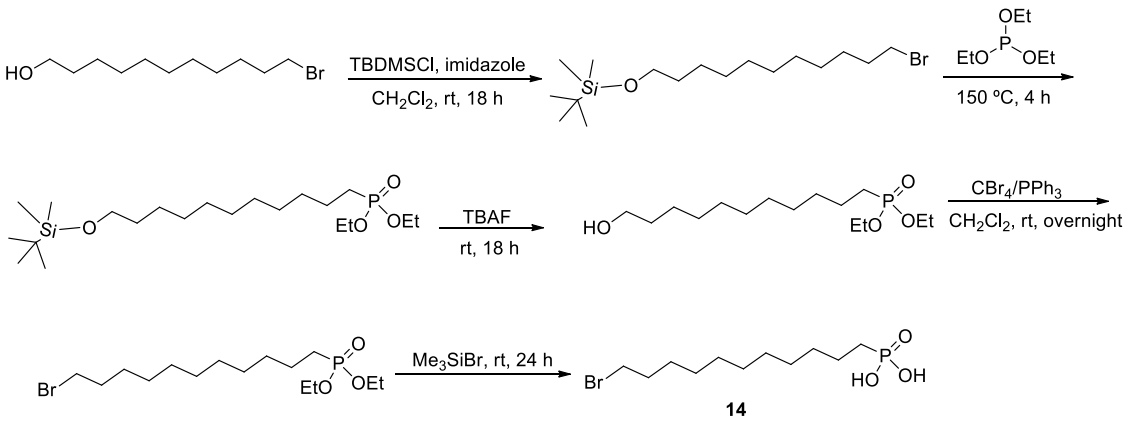
11-bromoundecyltriethoxysilane

This compound was prepared following a previously reported procedure.[4] 11-bromo-1-undecene 95% (0.376 mL, 1.64 mmol) was placed in a 10 mL Schlenk flask under an argon atmosphere and was dissolved in 0.5 mL of dry xylene. Triethoxysilane 95% (0.497 mL, 2.57 mmol) and Karstedt catalyst solution in xylene (2% in platinum) (0.982 mL, 0.086 mmol) were mixed together in another schlenk flask and the mixture was added to the 11-bromo-1-undecene solution *via* cannula. The reaction mixture was stirred overnight at 80 ºC. The reaction mixture was then cooled to room temperature, and on standing a dark solid precipitated. The solid was separated by filtration through a glass microfiber filter, and the solvent was removed under reduced pressure. The brown residue (0.405 g) was used without any further purification in the next step. All the spectroscopic data matched with those reported in the literature.[4] δ_H (400 MHz, $CDCl_3$) 3.90 (6 H, q, $^3J_{H\text{-}H}$ Hz, 7.0 Hz, -C*H*$_2$O-), 3.44 (2 H, t, $^3J_{H\text{-}H}$ 6.9, C*H*$_2$Br), 1.90 (2 H, m, C*H*$_2$CH$_2$N$_3$), 1.49–1.16 (24 H, m), 0.69 (2 H, m, SiC*H*$_2$).

11-Azidoundecyltriethoxysilane (8iii)

This compound was prepared following a previously reported procedure.[4] The reaction mixture from the preparation of 11-bromoundecyltriethoxysilane was transferred to a 25 mL Schlenk flask and 7 mL of dry acetonitrile were added. Then NaN_3 95.5% (0.166 g, 2.55 mmol) was added to the reaction medium as a solid. The reaction mixture was stirred at 90 ºC for 48 hours. The solvent was removed under reduced pressure, 20 mL dry pentane was added and the mixture was stirred for about 30 minutes. The white solid in suspension was separated by filtration *via* cannula and washed twice with 5 mL dry pentane. The filtrate together with the washings was evaporated to eliminate the solvent yielding **8iii** (0.31 g, 50% yield for the two combined steps) as clear yellowish oil. All the spectroscopic data matched with those reported in the literature.[4] ν_{max}/cm^{-1} 2971, 2925, 2855, 2095 (N_3), 1259, 1166,1104, 1080, 957; δ_H (400 MHz, $CDCl_3$) 3.82 (6 H, q, $^3J_{H\text{-}H}$ 7.0, -C*H*$_2$O-), 3.26 (2 H, t, $^3J_{H\text{-}H}$ 7.0, C*H*$_2$N$_3$), 1.60 (2 H, m, C*H*$_2$CH$_2$N$_3$), 1.27 (16 H, m), 1.23 (9 H, t, $^3J_{H\text{-}H}$ 7.0, C*H*$_3$), 0.65 (2 H, m, -SiC*H*$_2$-); δ_C (100.6 MHz, $CDCl_3$) 58.50 (*C*H$_2$CH$_3$), 51.72 (*C*H$_2$N$_3$), 33.40, 29.93, 29.76, 29.70, 29.45, 29.37, 29.06, 26.94, 22.97 (9 *C*H$_2$), 18.53 (*C*H$_3$), 10.61 (Si*C*H$_2$) ppm. *m/z* (ESI+) 382.1 ([M+Na]$^+$, 100 %)

3.2 Preparation of phosphonic acid derivative 14



(11-Bromoundecyloxy)(*tert*-butyl)dimethylsilane

This compound was prepared by slight modifications of a previously reported procedure.[5] A solution of 11-bromoundecan-1-ol (> 99%) (2.13 g, 8.50 mmol), *t*-butyldimethylsilyl chloride (1.41 g, 9.4 mmol) and imidazole 99.5% (1.27 g, 18.7 mmol) in dichloromethane (50 mL) was stirred at room temperature for 18 hours under nitrogen. Dichloromethane (50 mL) and NH_4Cl solution (50 mL) were added. The aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residual oil was purified by column chromatography on silica gel using hexane/ethyl acetate (97:3) as eluant to give the title compound (2.73 g, 88% yield) as a yellow oil. All the spectroscopic data matched with those reported in the literature.[5] δ_H (400 MHz, $CDCl_3$) 3.63 (2 H, t, $^3J_{H\text{-}H}$ 6.6, OCH_2), 3.43 (2 H, t, $^3J_{H\text{-}H}$ 6.1, CH_2Br), 1.86 (2 H, m), 1.54 (2 H, m), 1.45 (2 H, m), 1.29 (12 H, m), 0.91 (9 H, s, (CH_3)$_3$C), 0.06 (6 H, s, CH_3Si); δ_C (100 MHz, $CDCl_3$) 63.4 (O*C*H$_2$), 33.9, 33.0, 32.9, 29.7, 29.6, 29.5, 28.9, 28.3, 26.1, 25.9, 18.5, -5.15 (*C*H$_3$Si).

Diethyl 11-(tert-butyldimethylsilyloxy)undecylphosphonate

This product were prepared by slight modifications of a previously reported procedure.[6] (11-Bromoundecyloxy)(*tert*-butyl)dimethylsilane (2.735 g, 7.48 mmol) and triethyl

phosphite 98% (2.6 mL, 14.96 mmol) were heated at reflux at 150 ºC for 4 hours. Then the excess of triethyl phosphite was removed at reduced pressure to render the phosphonate product (3.00 g, 94% yield) as an oil. δ_H (400 MHz, $CDCl_3$) 4.07 (4 H, m, OCH_2CH_3), 3.58 (2 H, t, $^3J_{H\text{-}H}$ 6.6, CH_2OSi), 1.65 - 1.59 (4 H, m), 1.49 (2 H, m), 1.40 - 1.18 (20 H, m), 0.88 (9 H, s, $(CH_3)_3C$), -0.03 (6 H, s, CH_3Si); δ_C (MHz, $CDCl_3$) 63.2 (CH_2OSi), 61.3 (d, $^2J_{C\text{-}P}$ 6.4, CH_2CH_3), 32.9, 30.6, 30.5, 29.6, 29.5, 29.46, 29.41, 29.35, 29.33, 29.1, 26.4, 26.0, 25.8, 25.0, 22.47 (d, $J_{C\text{-}P}$ 5.2), 18.3, 16.55 (d, $^3J_{C\text{-}P}$ 6.0), -5.3 (CH_3Si); δ_P (162 MHz, $CDCl_3$) 35.7 (s).

Diethyl 11-(hydroxy)undecylphosphonate

This product were prepared by slight modifications of a previously reported procedure.[6] A sample of the phosphonate prepared in the previous step (2.97 g, 7.03 mmol) dissolved in 25 mL of tetrahydrofurane was treated with tetrabutylammonium fluoride (10.54 mmol, 10.54 mL of 1 M solution) for 18 hours. After this time, 25 mL of water were added. The product was extracted with dichloromethane (3 × 20 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The hidroxyphosphonate was obtained as an oil in quantitative yield. All the spectroscopic data matched with those reported in the literature.[6] δ_H (MHz, $CDCl_3$) 4.06 (4 H, m, OCH_2CH_3), 3.63 (2 H, t, $^3J_{H\text{-}H}$ 6.7), 2.5 (1 H, br s, OH), 1.79-1.51 (6 H, m), 1.40-1.23 (20 H, m); δ_P (162 MHz, $CDCl_3$) 35.8 (s).

Diethyl 11-bromoundecylphosphonate

To a solution of the hydroxyphosphonate prepared in the previous step (1.58 g, 5.10 mmol) and CBr_4 (2.04 g, 6.00 mmol) in dichloromethane (25 mL) at 0 ºC, PPh_3 was added (1.64 g, 6.25 mmol). The reaction was stirred overnight and then, 5 mL of ethanol were added. After 2 hours, the addition of 20 mL of diethyl ether at low temperature produces the precipitation of a white solid. The solid was discarded and the organic solution was concentrated at reduced pressure. The crude product was purified by column chromatography on silica gel eluting with hexane/ethyl acetate mixtures (from 20% to 50% in ethyl acetate) to render the bromophosphonate (1.51 g, 80% yield)

as a white solid. δ_H (400 MHz, $CDCl_3$) 4.20 - 3.98 (4 H, m, OCH_2CH_3), 3.41 – 3.35 (2 H, m), 1.88 – 1.77 (2 H, m), 1.77 – 1.64 (2 H, m,), 1.63 – 1.49 (2 H, m), 1.48 – 1.16 (20 H, m); δ_C (100.6 MHz, $CDCl_3$) 60.9 (d, $^2J_{C\text{-}P}$ 6.5, OCH_2CH_3), 33.1 (CH_2Br), 32.1, 29.9, 29.7, 28.7, 28.65, 28.56, 28.3, 27.9 27.4, 25.6, 24.2, 21.7 (d, *J* 5.9), 15.8 (d, $^3J_{C\text{-}P}$ 5.9, OCH_2CH_3); δ_P (162 MHz, $CDCl_3$) δ 35.7.

11-Bromoundecylphosphonic acid (14)

This product were prepared by slight modifications of a previously reported procedure.[7] Diethyl 11-bromoundecylphosphonate (1.06 g, 2.87 mmol) was stirred in 15 mL of Me_3SiBr (115 mmol) at room temperature for 24 hours. The volatiles were then removed and the residue was dissolved in a mixture 11 mL of tetrahydrofurane and 4 mL of H_2O, stirred for 1 hour and finally concentrated *in vacuo*. Product **14** (0.599 g, 66% yield) was obtained as a white solid after addition of 15 mL of $CHCl_3$. Found: C, 42.09; H, 7.91; Br, 24.14 %. Calc for $C_{11}H_{24}BrO_3P$: C, 41.92; H, 7.68; Br, 25.35 %; ν_{max}/cm^{-1} 2917, 2850, 1467, 1224, 1077, 1001, 958; δ_H (400 MHz, CD_3OD) 3.45 (2 H, t, $^3J_{H\text{-}H}$ 6.7, CH_2Br), 1.91 – 1.76 (2 H, m), 1.74 – 1.53 (4 H, m), 1.50 – 1.36 (4 H, m), 1.36 – 1.25 (10 H, m); δ_C (100.6 MHz, CD_3OD) 34.6 (CH_2Br), 34.1, 31.9, 31.8, 30.68, 30.65, 30.57, 30.4, 29.9, 29.3, 29.0, 27.5, 24.0 (d, *J* 4.9); δ_P (162 MHz, CD_3OD) 37.4.

3.3 Preparation of azido-magnetite nanoparticles 9i-9iii

The following procedures describe the preparation of nanoparticles **9ii-9iii**. The preparation of nanoparticles **9i**, involving the use of **8i**, is described in the main text.

Magnetite nanoparticles functionalised with 5-azidopentyltriethoxysilane (9ii)

These nanoparticles were prepared by slight modifications of a previously reported procedure.[8] Nanoparticles **7** (0.20 g) were dispersed in 90 mL dry and degassed toluene. Compound **8ii** (0.35 g, 1.288 mmol) was added to the suspension of nanoparticles, then glacial acetic acid *d* = 1.05 g/mL (0.026 mL, 0.0275 g, 0.458 mmol) and finally water (0.056 mL, 3.1 mmol). The reaction was heated to 100 ºC for 24 hours. After cooling to room temperature, the brown particles were allowed to settle over the weekend. Then,

the supernatant was separated *via* cannula and the nanoparticles were washed three times with 2 mL toluene and three times with 3 mL of methanol (HPLC grade) and dried with an argon stream. In this manner, 0.133 g of nanoparticles were isolated with a particle size of 8.17 nm (s = 4.14). According to the %N determined by elemental analysis the functionalisation of the nanoparticles was f = 0.297 mmol N_3/g. Elemental analysis found C, 6.12; H, 1.15; N, 1.25 %. ν_{max}/cm^{-1} 3443, 2960, 2926, 2852, 2096 (N_3), 1631, 1433, 1261, 1051, 632, 585. TGA (30 - 1000 ºC, 10 ºC/min, under N_2; for a 3.0130 mg sample, % weight loss) 9.6690 (onset: 182.59 ºC), 9.1219 (onset: 608.68 ºC).

Magnetite nanoparticles functionalised with 11-azidoundecyltriethoxysilane (9iii)

These nanoparticles were prepared by slight modifications of a previously reported procedure.[8] Nanoparticles **7** (0.15 g) were dispersed in 50 mL dry and degassed toluene. Compound **8iii** (0.272 g, 0.76 mmol) was added to the suspension of nanoparticles, then glacial acetic acid 99.5% d = 1.05 g/mL (0.0165 mL, 0.0173 g, 0.2881 mmol,) and finally water (0.042 mL, 2.3 mmol). The reaction mixture was heated to 100 ºC for 24 hours, stirred with a shaker. After cooling to room temperature, the red-brown particles were allowed to settle over the weekend. Then, the supernatant was separated *via* cannula and the nanoparticles were washed three times with 3 mL toluene and three times with 3 mL of methanol (HPLC grade) and dried with an argon stream. 0.110 g of nanoparticles were isolated with a particle size of 10.15 nm (s = 3.01). According to the %N determined by elemental analysis a functionalisation of the nanoparticles of f = 0.233 mmol N_3/g was achieved. Elemental analysis found: C, 6.72; H, 1.32; N, 0.98 %. ν_{max}/cm^{-1} 3445, 2925, 2853, 2094 (N_3), 1634, 1429, 1258, 1053, 630, 588. TGA (30-1000 ºC, 10 ºC/min, under N_2; for a 5.3060 mg sample, % weight loss) 10.0213(left limit: 124.28 ºC; right limit: 522.10 ºC), 5.4580 (left limit: 522.82 ºC; right limit: 737.35 ºC), 4.3083 (left limit: 737.35 ºC; right limit: 900.16 ºC).

3.4 CuAAC reactions for the preparation of functional MNPs

The following procedure describes the preparation of nanoparticles **11bi**. The procedure for the preparation of the analogous MNPs **11ai**, involving the use of the crown ether derivative **10a**, is described in the main text.

CuAAC reaction of aza-crown ether derivative 10b with magnetite nanoparticles 9i: preparation of nanoparticles 11bi

Magnetite nanoparticles **9i** (40 mg, *f* = 1.77 mmol of N_3/g) were dispersed in 4 mL of anhydrous DMF in a Schlenk flask under argon, using ultrasonication for 15 min to ensure dispersion. The alkyne **10b** (0.0427 g, 0.142 mmol) dissolved in 0.5 mL anhydrous DMF was then added to the reaction media, followed by DIPEA 99.5% (0.125 mL, 0.0926 g, 0.716 mmol), and finally copper(I) iodide (7.6 mg, 0.0398 mmol) as a solid. The reaction mixture was magnetically stirred at 40 ºC, under argon. After 4 days, the reaction was cooled to room temperature, the solvent was removed *in vacuo*, MeOH was added (2 mL), and the mixture was left for a few hours in the freezer. The precipitating particles were collected using an external magnet. The supernatant was separated by centrifugation and the particles were dried under an argon stream. When IR spectroscopy showed the disappearance of the azido signal, complete reaction was assumed. In this manner, 18.4 mg of functional magnetite nanoparticles were obtained with a particle size of 8.11 nm (*s* = 1.56). According to the %N determined by elemental analysis the functionalisation of the nanoparticles was *f* = 0.604 mmol/g. Elemental analysis found: C, 17.53; H, 2.69; N, 3.38. ν_{max}/cm^{-1} 3453, 2917, 1631, 1453, 1352, 1248, 1106, 951, 834. TGA (30 - 900 ºC, 10 ºC/min, under N_2; for a 3.167 mg sample, % weight loss) 20.4693 (left limit: 168.67 ºC, right limit: 451.44 ºC), 26.8379 (left limit: 451.44 ºC, right limit: 852.86 ºC).

CuAAC reaction of crown ether derivative 10a with magnetite nanoparticles 9ii: preparation of nanoparticles 11aii

Magnetite nanoparticles **9ii** (60 mg, *f* = 0.297 mmol of N_3/g) were dispersed in 4 mL of anhydrous DMF in a schlenk flask under argon, using ultrasonication for 15 min to achieve dispersion. The alkyne **10a** (17 mg, 0.0511 mmol), dissolved in 2 mL anhydrous DMF was then added to the reaction media, followed by DIPEA 99.5 % (0.056 mL, 41.0 mg, 0.320 mmol), and finally copper(I) iodide (1.9 mg, 0.0099 mmol) as a solid. The reaction mixture was magnetically stirred at 40 ºC under argon. After 6 days, the reaction was cooled to room temperature, methanol was added (50 mL), and the mixture was left overnight in the freezer. The precipitating particles were separated by magnetic decantation. The supernatant was discarded and the particles were washed

with methanol (2 × 5 mL), distilled water (2 × 2 mL) and methanol again (2 × 5 mL) using centrifugation for particle settling. The particles were dried under an argon stream. When IR spectroscopy showed the disappearance of the azido signal, complete reaction was assumed. In this manner 45.5 mg of functional magnetite nanoparticles were obtained with a particle size of 9.88 nm (*s* = 3.2). According to the %N determined by elemental analysis a functionalisation of the nanoparticles of *f* = 0.248 mmol/g was determined. Elemental analysis found: C, 7.59; H, 1.48, N, 1.04. ν_{max}/cm^{-1} 3444, 2923, 1632, 1451, 1352, 1256, 1106, 632, 581. TGA (30 - 1000 ºC, 10 ºC/min, under N_2; for a 3.8660 mg sample, % weight loss) 13.6315 (onset: 250.81 ºC), 4.7465 (left limit: 514.28 ºC, right limit: 728.77 ºC), 3.7260 (left limit: 728.06 ºC, right limit: 896.59 ºC).

CuAAC reaction of aza-crown ether derivative 10b with 9ii: preparation of nanoparticles 11bii

Magnetite nanoparticles **9ii** (47.9 mg, *f* = 0.297 mmol of N_3/g) were dispersed in 3 mL of anhydrous DMF in a schlenk flask under argon, using ultrasonication for 15 minutes. The alkyne **10b** (10.3 mg, 0.0341 mmol), dissolved in 2 mL anhydrous DMF was then added to the reaction media, followed by DIPEA 99.5% (0.0445 mL, 33.0 mg, 0.2553 mmol), and finally copper(I) iodide (1.1 mg, 0.0057 mmol) as a solid. The reaction mixture was magnetically stirred at 40 ºC under argon. After 7 days, the reaction mixture was cooled to room temperature, methanol was added (50 mL), and the mixture was left overnight in the freezer. The precipitating particles were separated by magnetic decantation. The supernatant was discarded and the particles were washed with methanol (2 × 5 mL), distilled water (2 × 2 mL) and methanol again (2 × 5 mL) and dried with an argon stream. When IR spectroscopy showed the disappearance of the azido signal, complete reaction was assumed. In this manner 26.7 mg of functional magnetite nanoparticles were obtained with a particles size of 9.23 nm (*s* = 2.82). According to the %N determined by elemental analysis the functionalisation of the nanoparticles was *f* = 0.234 mmol/g. Elemental analysis found C, 7.90; H, 1.44; N, 1.31. ν_{max}/cm^{-1} 3422, 2923, 2850, 1633, 1455, 1353, 1251, 1106, 952, 633, 588. TGA (30 – 1000 ºC, 10 ºC/min, under N_2; for a 3.9970 mg sample, % weight loss) 13.7333 (left limit: 147.00 ºC, right limit: 513.07 ºC), 8.0758 (left limit: 512.34 ºC, right limit: 832.66 ºC).

CuAAC reaction of crown ether 10a with magnetite nanoparticles 9iii: preparation of nanoparticles 11aiii

Magnetite nanoparticles **9iii** (60 mg, *f* = 0.233 mmol of ligand/g) were dispersed in 4 mL of anhydrous DMF in a Schlenk flask under argon, using ultrasonication for 10 min to ensure dispersion. The alkyne **10a** (19.6 mg, 0.058 mmol), dissolved in 1.5 mL anhydrous DMF was then added to the reaction media, followed by DIPEA 99.5% (0.0636 mL, 0.0472 g, 0.365 mmol), and finally CuI (1.6 mg, 0.008 mmol) as a solid. The reaction mixture was magnetically stirred at 40 ºC under argon. After 10 days, the reaction mixture was cooled to room temperature, the solvent was evaporated in the vacuum line to about one half of its volume, methanol was added (c.a. 30 mL), and the mixture was left for 2 hours in the freezer. The precipitating particles were separated by magnetic decantation. The supernatant was discarded and the particles were washed with methanol (3 × 10 mL), distilled water (2 × 5 mL) and methanol again (2 × 5 mL) and dried with an argon stream. When IR spectroscopy showed the disappearance of the azido signal, complete reaction was assumed. In this manner, 45.5 mg of magnetite nanoparticles were obtained with a mean particle size of 10.19 nm (*s* = 3.23). According to the %N determined by elemental analysis the functionalisation of the nanoparticles was *f* = 0.188 mmol/g. Elemental analysis found: C, 8.45; H, 1.52; N, 0.79. ν_{max}/cm^{-1} 3441, 2923, 2853, 1636, 1458, 1352, 1252, 1105, 632, 585. TGA (30 – 1000 ºC, 10 ºC/min, under N_2; for a 4.1060 mg sample, % weight loss) 8.2165 (left limit: 122.02 ºC, right limit: 332.93 ºC), 5.1135 (left limit: 339.25 ºC, right limit: 538.31 ºC), 9.1556 (left limit: 538.31 ºC, right limit: 873.95 ºC).

CuAAC reaction of aza crown ether derivative 10b with magnetite nanoparticles 9iii: preparation of nanoparticles 11biii

Magnetite nanoparticles **9iii** (37.7 mg, *f* = 0.233 mmol of N_3/g) were dispersed in 3 mL of anhydrous DMF in a Schlenk flask under argon, using ultrasonication for 15 min to ensure dispersion. The alkyne **10b** (12.6 mg, 0.041 mmol), dissolved in 1.5 mL anhydrous DMF was then added to the reaction media, followed by DIPEA 99.5% (0.0276 mL, 20.5 mg, 0.1586 mmol), and finally CuI (0.7 mg, 0.0035 mmol) as a solid. The reaction mixture was stirred using a magnetical stirring bar at 40 ºC under argon.

After 5 days, the reaction mixture was cooled to room temperature, the solvent was evaporated in the vacuum line to about one half of its volume, methanol was added (c.a. 40 mL), and the mixture was left for 2 hours in the freezer. The precipitating particles were collected using an external magnet. The supernatant was discarded and the particles were washed with methanol (3 × 10 mL), distilled water (2 × 5 mL) and methanol again (2 × 10 mL) and dried under an argon stream. IR showed no azide band, so complete reaction was assumed. In this manner, 30.9 mg of magnetite nanoparticles were obtained with a mean particle size of 10.80 nm (s = 2.71). According to the %N determined by elemental analysis the functionalisation of the nanoparticles was f = 0.212 mmol/g. Elemental analysis found: C, 8.47; H, 1.56; N, 1.19. ν_{max}/cm^{-1} 3443, 2922, 2852, 1650, 1458, 1355, 1256, 1106, 953, 632, 587. TGA (30 – 1000 ºC, 10 ºC/min, under N_2; for a 3.7770 mg sample, % weight loss) 7.8333 (left limit: 137.22 ºC, right limit: 333.88 ºC), 5.5089 (left limit: 333.88 ºC, right limit: 513.79 ºC), 4.2949 (left limit: 512.35 ºC, right limit: 728.41 ºC), 4.2519 (left limit: 729.13 ºC, right limit: 802.71 ºC).

CuAAC reaction of phenylacetylene with magnetite nanoparticles: preparation of nanoparticles 12

Magnetite nanoparticles **9i** (0.3 g, f = 0.35 mmol of N_3/g) were dispersed in 1 mL of a 1:1 H_2O/CH_3CN mixture, using ultrasonication for 5 minutes to ensure dispersion. Phenylacetylene 98% (24 μL, 0.216 mmol) was added to the mixture with a syringe, followed by tris(1-benzyl-1*H*-1,2,3-triazol-4-yl)methanol·CuCl catalyst[1] (2.6 mg, 4.3 μmol) as a solid. The reaction mixture was shaken at room temperature for 5 days, checking periodically the progress of the reaction by IR spectroscopy. The precipitating particles were separated by magnetic decantation. The supernatant was discarded and the particles were washed with acetonitrile (3 × 5 mL) and methanol (3 × 5 mL). The nanoparticles were dried under an argon stream. In this manner 0.29 g of nanoparticles were obtained with a mean particle size of 9.86 nm (s = 2.82). According to the %N determined by elemental analysis a functionalisation of the nanoparticles of f = 0.32 mmol ligand/g was achieved. Elemental analysis found: C, 6.25; H, 0.87; N, 1.35. ν_{max}/cm^{-1} 3427, 2924, 2851, 1633, 1432, 1227, 1100, 1049 (sh), 582. TGA (30 - 900 ºC,

[1] The tris(1-benzyl-1*H*-1,2,3-triazol-4-yl)methanol·CuCl catalyst was prepared according to *Org. Lett*, **2009**, 11, 4690.

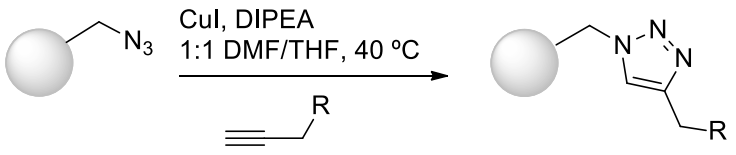
10 ºC/min, under N_2; for a 2.8420 mg sample, % weight loss) 12.2540 (left limit: 37.92 ºC; right limit 514.87 ºC), 6.5469 (left limit: 514.87 ºC; right limit 835.03 ºC).

CuAAC reaction between functional magnetite nanoparticles 16 and alkyne 10b: Synthesis of hybrid nanoparticles 17b

Magnetite nanoparticles **16** (55.5 mg, f = 2.16 mmol N_3/g) were dispersed in 5 mL dry DMF in a Schlenk flask under an argon atmosphere. The alkyne **10b** (72.3 mg, 0.24 mmol), dissolved in 1 mL dry DMF was added to the suspension of the nanoparticles, followed by DIPEA 99.5% (0.27 mL, 201.4 mg, 1.53 mmol), and finally copper(I) iodide (1.8 mg, 0.0096 mmol) as a solid. The reaction mixture was magnetically stirred at 40 ºC under argon for 4 days. The progress of the reaction was followed by IR spectroscopy, taking a small sample of the reaction mixture. From this sample, the nanoparticles were precipitated with methanol, centrifuged, washed once with methanol (about 2 mL) and analysed by IR spectroscopy. If required, additional amounts of CuI and alkyne were added. The reaction mixture was cooled to room temperature, 35 mL methanol (HPLC grade) were added and the mixture was centrifuged (15 minute, 4400 rpm) and the supernatant was separated using a pipette. The particles were washed four times with 5 mL methanol, using centrifugation and were dried under an argon stream. In this manner 25.1 mg of nanoparticles were isolated as a brown solid with a mean particle size of 5.58 nm (s = 1.07). According to the %N determined by elemental analysis the functionalisation of the nanoparticles was f = 1.27 mmol/g. Elemental analysis found: C, 43.55; H, 7.19; N, 7.13. ν_{max}/cm^{-1} 3424, 3125, 2921, 2851, 1641, 1467, 1354, 1249, 1219, 1109, 1050, 952, 836, 787, 717. TGA (30 – 1000 ºC, 10 ºC/min, under N_2; for a 3.5520 mg sample, % weight loss): 35.4799 (left limit: 125.85 ºC, right limit: 418.29 ºC), 20.8361 (onset: 460.99 ºC), 15.1357 (onset: 884.46 ºC).

The preparation of nanoparticles **17a** from MNPs **16** and alkyne **10a** is described in the main text.

4 PREPARATION OF FUNCTIONALISED POLYMERS



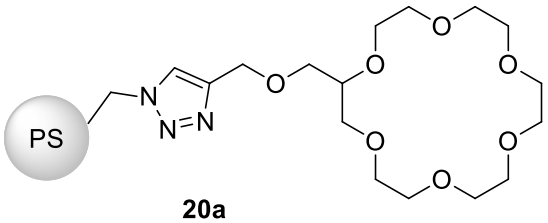
10a, **10b**

18 = PS beads

19 = PS-PEG beads

20a-b = PS beads

21a-b = PS-PEG beads



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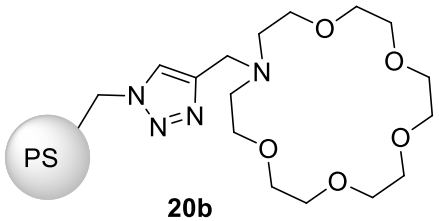

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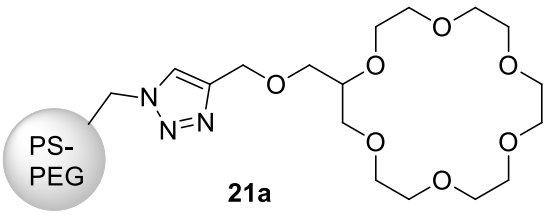

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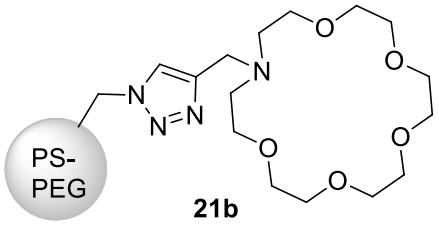

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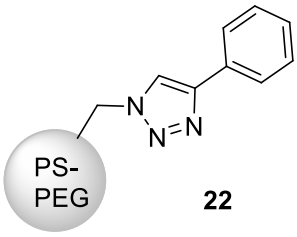


22

Preparation of (azidomethyl)polystyrene (18)

This product was prepared according to a previously reported procedure.[9]

Preparation of azido-polystyrene-polyethyleneglycol (19)

This product was prepared according to a previously reported procedure.[10]

CuAAC reaction between (azidomethyl)polystyrene (18) and alkyne 10b: preparation of polystyrene resin 20b

Alkyne **10b** (0.163 g, 0.54 mmol), DIPEA 99.5% (0.618 mL, 3.55 mmol) and copper(I) iodide (0.0064 g, 0.0328 mmol) were added to a suspension of 0.374 g (azidomethyl)polystyrene (f = 0.73 mmol/g) in 1:1 DMF/THF (3 mL) at 40 ºC for 72 hours. The reaction mixture was monitored and once the IR-signal of the azido group had completely disappeared, the resin was collected by filtration and sequentially washed with water (120 mL), THF (60 mL), MeOH (60 mL) and THF (60 mL). The solid was dried *in vacuo* for 24 hours at 40 ºC to obtain 0.28 g of resin. According to the %N determined by elemental analysis a functionalisation of f = 0.596 mmol/g of resin was achieved. Elemental analysis found: C, 82.36; H, 7.89; N, 3.34. ν_{max}/cm^{-1} 3059, 3025, 2920, 2852, 1945, 1719, 1601, 1492, 1452, 1351, 1118, 1065, 1029, 907, 843, 757, 698, 537. δ_H (500 MHz, CD_2Cl_2) 7.55 (H-triazole), 7.13 (s, br), 6.66 (s, br), 5.44, 3.86 (2 H, s), 3.74 (2 H, m) 3.65 (20 H, s, -(-CH_2-O-CH_2)$_5$-), 2.79, 1.87 (s, resin backbone), 1.49 (s, resin backbone); δ_C (126 MHz, CD_2Cl_2) 146.0, 128.58, 128.2, 126.3, 111.30, 71.2, 71.0, 70.7, 70.09, 68.31, 50.6, 46.6, 44.7, 40.99, 30.3, 26.1.

The preparation of resin **20a** from (azidomethyl)polystyrene and alkyne **10a** is described in the main text.

CuAAC reaction between azido-polystyrene-polyethyleneglycol (19) and alkyne 10b: preparation of polystyrene-polyethyleneglycol resin 21b

Alkyne **10b** (0.034 g, 0.113 mmol) dissolved in 1:1 DMF/THF (3 mL), DIPEA 99.5% (0.17 mL, 0.975 mmol) and copper(I) iodide (0.0018 g, 0.009 mmol) were added to a

suspension of azido-terminated polystyrene–polyethyleneglycol (0.3 g, *f* = 0.25mmol/g) and 1:1 DMF/THF (3 mL) at 40 ºC and the mixture was shaken for 24 hours. The progress of the reaction was monitored and once the IR-signal of the azido group had completely disappeared, the resin was collected by filtration and sequentially washed with water (80 mL), DMF (80 mL), THF (80 mL), 1:1 THF/MeOH (80 mL), MeOH (80 mL) and THF (80 mL). The solid was dried *in vacuo* for 24 hours at 40 ºC to obtain 0.210 g of resin. According to the %N determined by elemental analysis a functionalisation of *f* = 0.218 mmol/g of resin was achieved. Elemental analysis found C, 63.18; H, 8.49; N, 1.22; ν_{max}/cm^{-1} 3026, 2864, 1638, 1602, 1492, 1453, 1343, 1280, 1242, 1099, 947, 842, 761, 701; δ_H (500 MHz, CD_2Cl_2) 7.76 (1 H, s, triazole), 7.07 (s, br, polymer backbone), 6.55 (s, br, polymer backbone), 4.55 (2 H, s), 3.32-4.09 (resin backbone + macrocycle), 2.77 (4 H, s), 1.77 (s, polymer backbone), 1.30; δ_C (126 MHz, CD_2Cl_2) 145.3 128.5, 111.2, 85.3, 71.9, 70.8, 70.5, 69.7, 50.5, 40.9.

The preparation of resin **21a** from azido-terminated polystyrene–polyethyleneglycol and alkyne **10a** is described in the main text.

CuAAC reaction between azido-polystyrene-polyethyleneglycol (19) and phenyl acetylene: preparation of polystyrene-polyethyleneglycol resin 22

Ethynylbenzene 98% (0.011 mL, 0.010 g, 0.10 mmol), DIPEA 99.5% (0.113 mL, 0.650 mmol) and copper(I) iodide (0.0012 g, 0.006 mmol) were added to a suspension of 0.2 g of azidopolystyrene–polyethyleneglycol (*f* = 0.25 mmol/g) in 1:1 DMF/THF (5 mL) at 40 ºC and the mixture was shaken for 24 hours. The progress of the reaction was monitored and once the IR signal of the azido group had completely disappeared, the resin was collected by filtration and sequentially washed with water (55 mL), DMF (50 mL), THF (50 mL), 1:1 THF/MeOH (50 mL), MeOH (50 mL) and THF (50 mL). The solid was dried *in vacuo* for 24 hours at 35 ºC to afford 0.157 g of resin. According to the %N determined by elemental analysis a functionalisation of *f* = 0.24 mmol/g of resin was achieved. Elemental analysis found C, 63.87; H, 8.22; N, 1.01. ν_{max}/cm^{-1} 3026, 2865, 1602, 1492, 1453, 1345, 1281, 1244, 1096, 947, 842, 762, 700, 538.

5 IR SPECTRA OF FUNCTIONALISED POLYMERS

Figure S1 IR spectrum of polymers **18** and **20a**. For comparison the spectrum of compound **10a** was included.

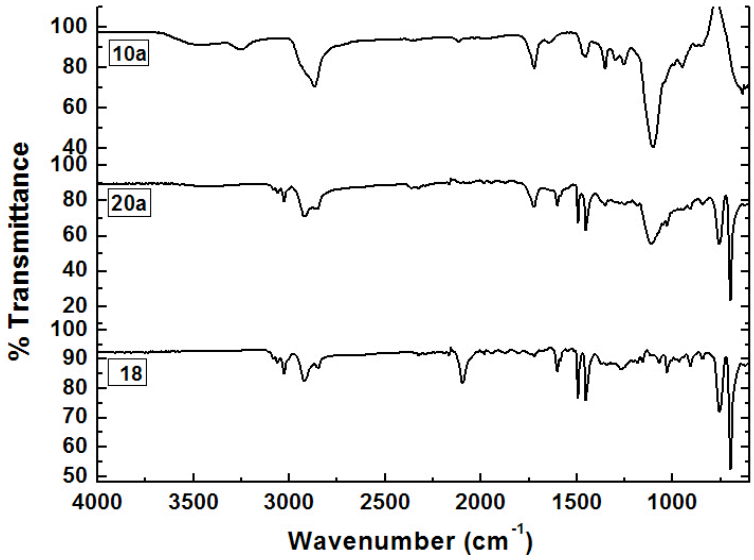
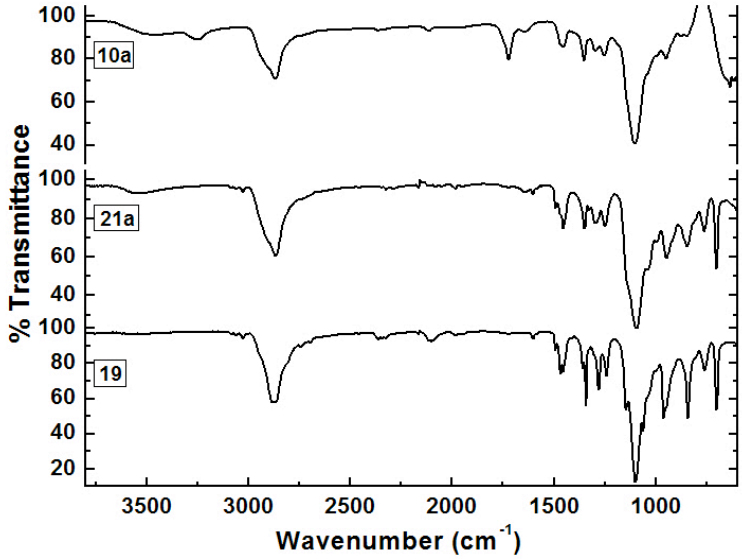
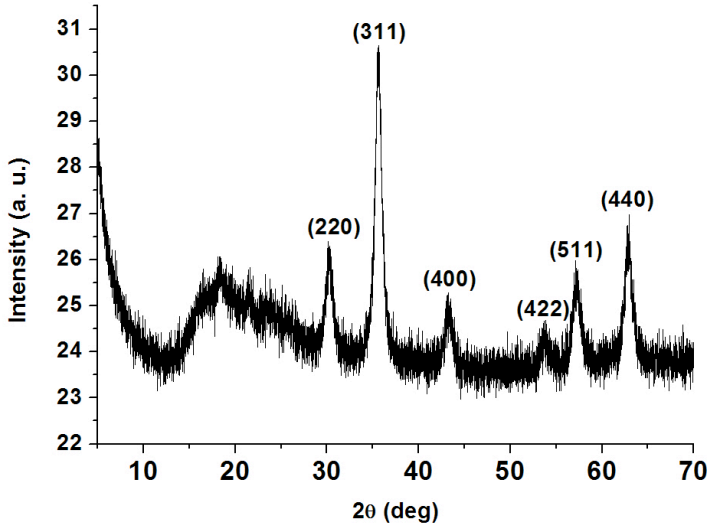


Figure S2 IR spectrum of polymers **19** and **21a**. For comparison the spectrum of compound **10a** was included.



6 XRD SPECTRA OF NANOPARTICLES

Figure S3 XRD spectrum of the MNPs **7**.



7 TGA CURVES OF NANOPARTICLES

Figure S4 TGA curves for oleic acid nanoparticles **7**, nanoparticles after grafting with ω-azidoalkyltrialkoxysilane **9ii**, and nanoparticles after CuAAC reaction **11aii** and **11bii**.

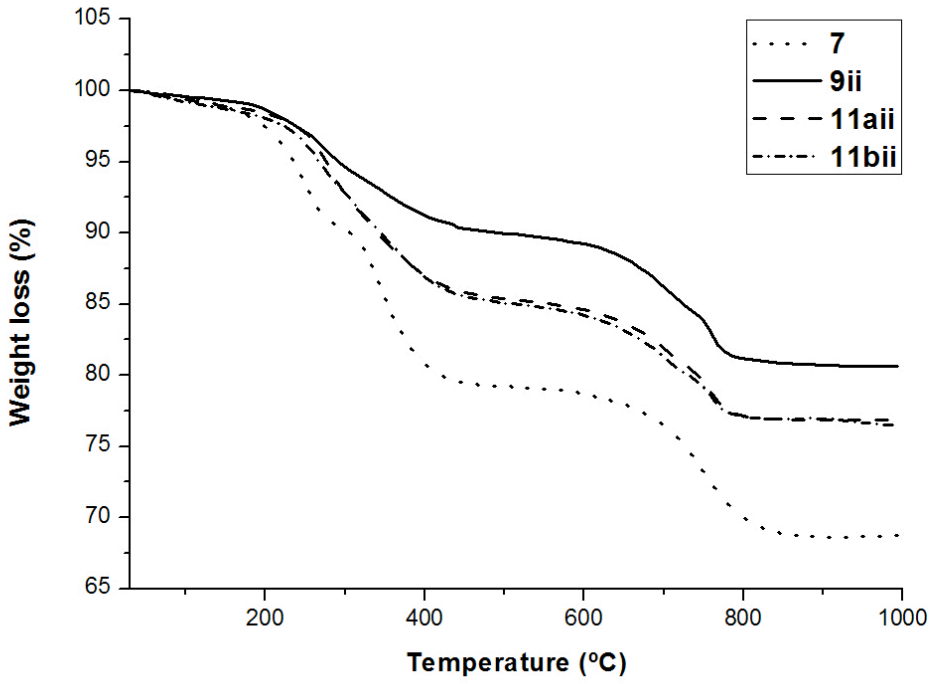
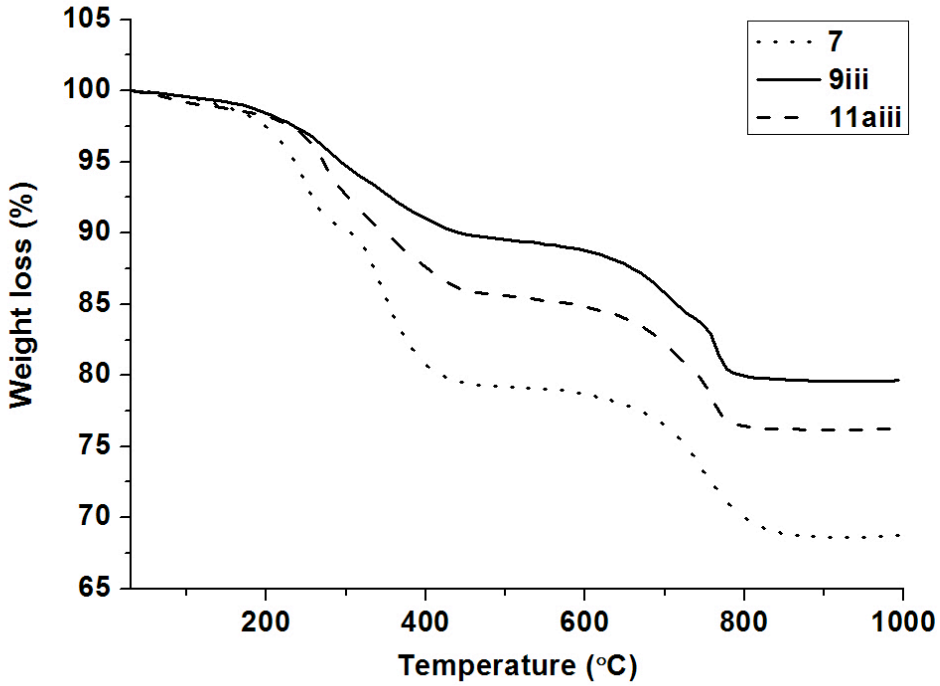


Figure S5 TGA curves for oleic acid nanoparticles **7**, nanoparticles after grafting with ω-azidoalkyltrialkoxysilane **9iii**, and nanoparticles after CuAAC reaction **11aiii**.



8 TEM IMAGES OF MAGNETIC NANOPARTICLES

Figure S6 TEM images of cobalt nanoparticles **6d** (a) and Fe_3O_4 MNPs **12** (b).

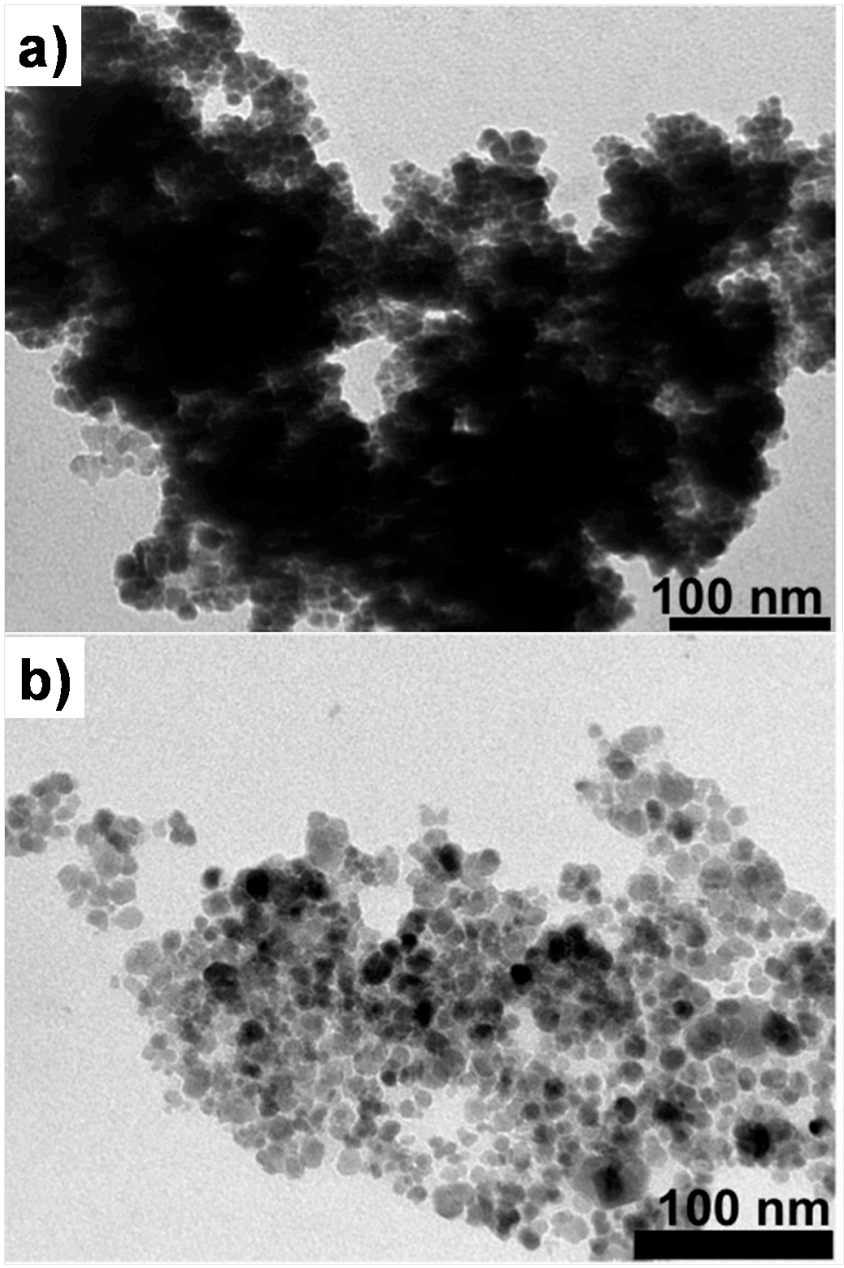


Figure S7 TEM image for MNPs of Fe_3O_4 a) **9ii**; b) **9iii**; c) **11aii**; d) **11bii**; e) **11aiii**; f) **11biii**.

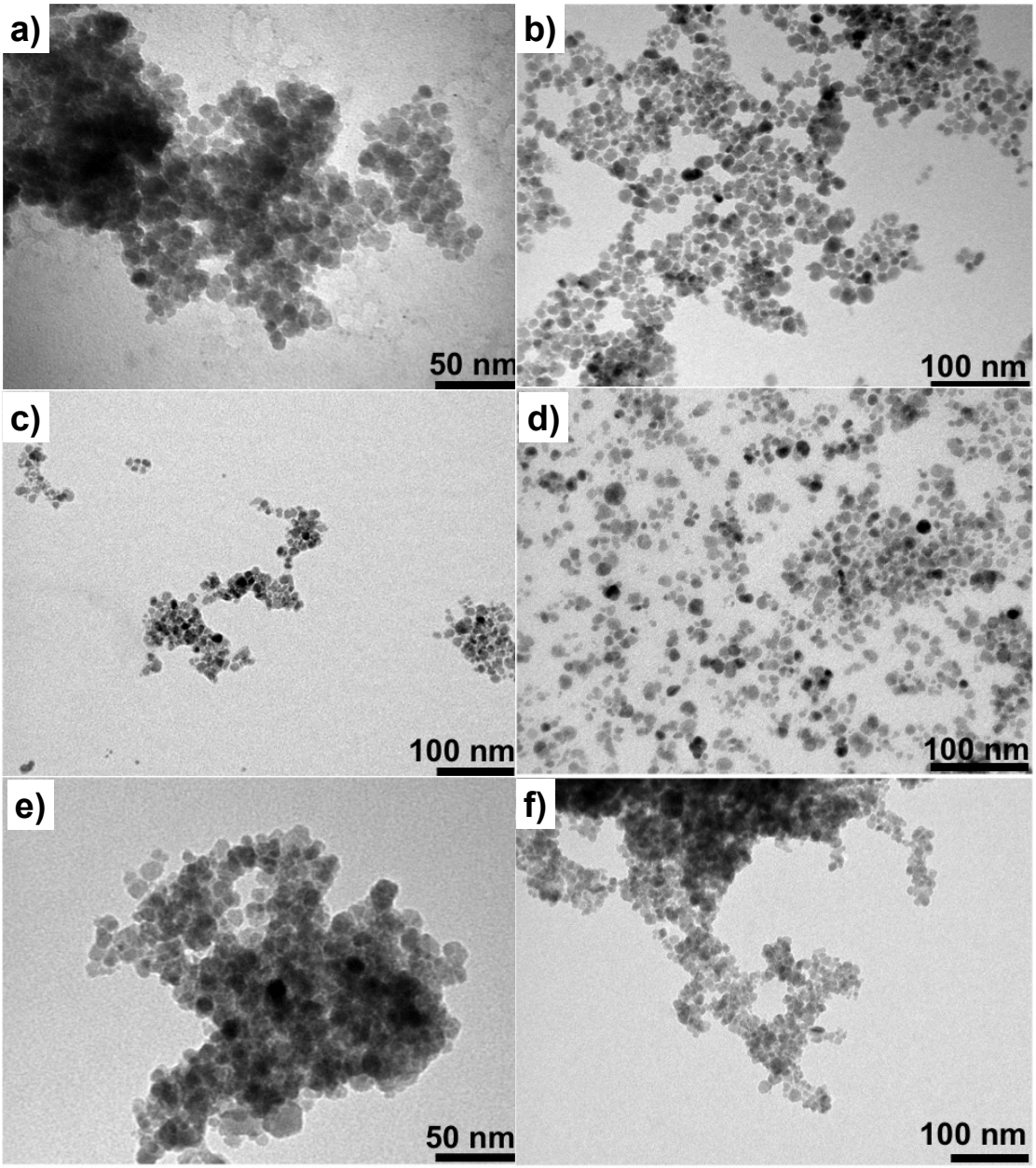
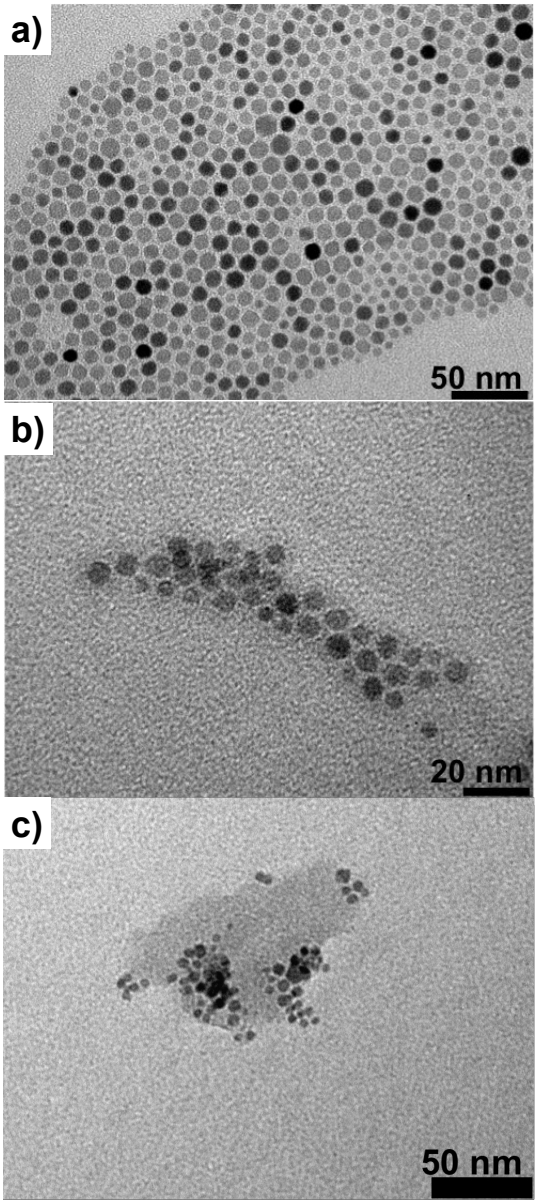


Figure S8 TEM images of MNPs of Fe_3O_4 a) **13**; b) **15** and c) **16**.



9 SIZE DISTRIBUTION DIAGRAMS FOR MAGNETITE NANOPARTICLES

Figure S9 Size distribution for MNPs **7**, **11ai** and **11bi**.

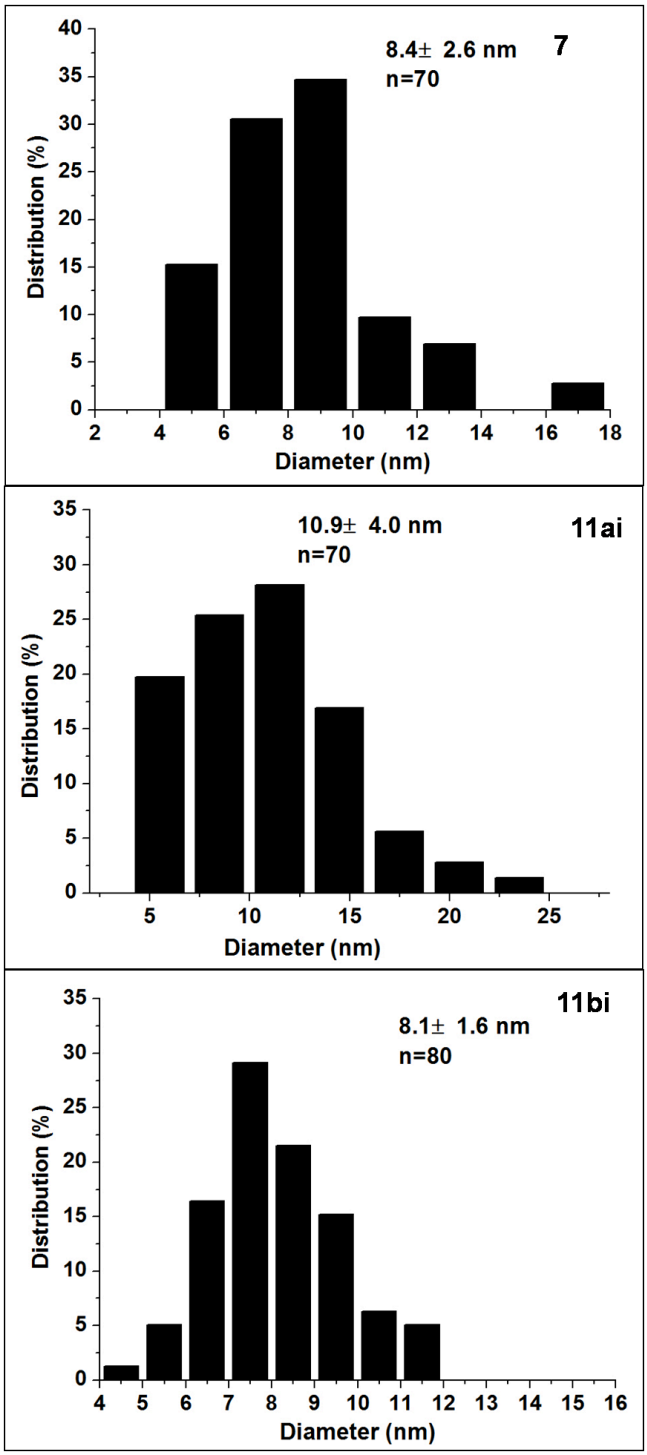
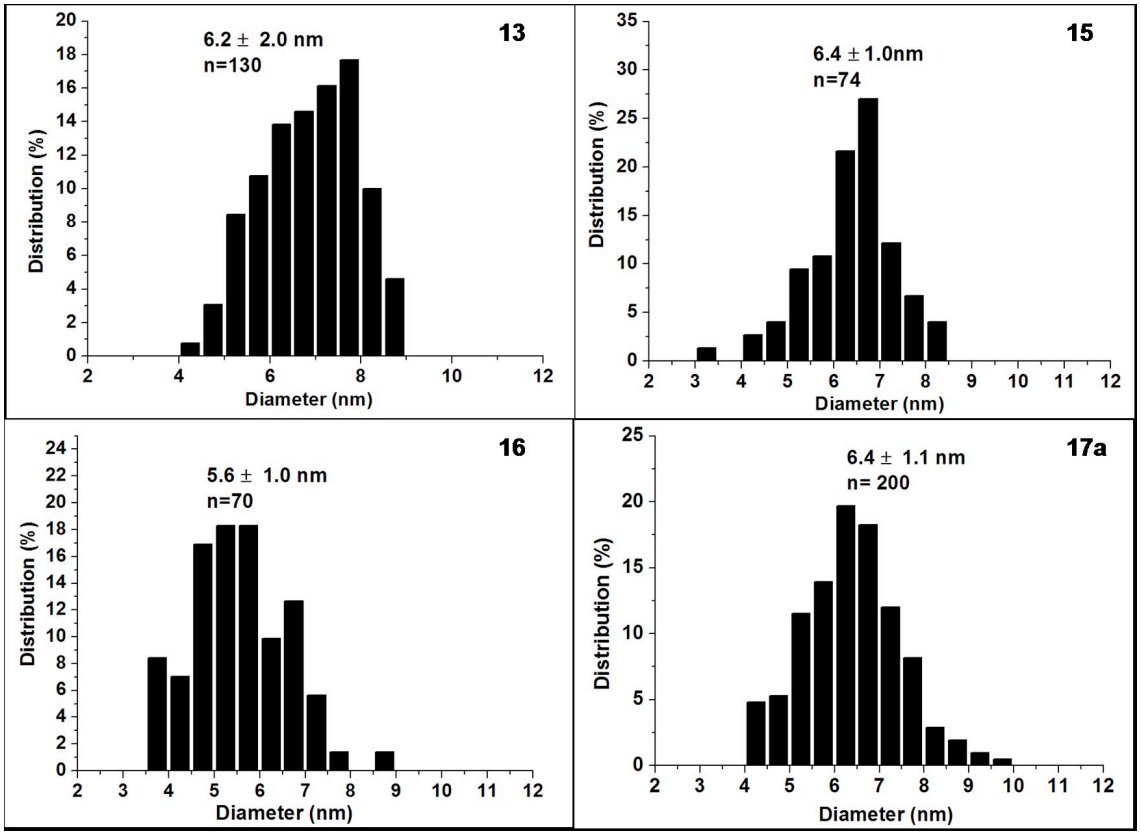


Figure S10 Size distribution for MNPs **13**, **15**, **16** and **17a**.



10 REFERENCES

1 K. S. Moon, E. Lee, Y. B. Lim and M. Lee, *Chem. Commun.*, 2008, 4001.

2 (a) W. P. Heal, S. R. Wickramasinghe, P. W. Bowyer, A. A. Holder, D. F. Smith, R. J. Leatherbarrow and E. W. Tate, *Chem. Commun.*, 2008, 480; (b) V. Neto, R. Granet and P. Krausz, *Tetrahedron*, 2010, **66**, 4633.

3 C. A. Bradley, B. D. Yuhas, M. J. McMurdo and T. D. Tilley, *Chem. Mater.*, 2009, **21**, 174.

4 B. P. Pichon, M. Wong Chi Man, C. Bied and J. J. E. Moreau, *J. Organomet. Chem.*, 2006, **691**, 1126.

5 J. R. Carlise and M. Weck, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 2973; (x) N. Mizoshita and T. Kato, *Adv. Funct. Mater.*, 2006, **16**, 2218.

6 H. J. Deussen, S. Danielsen, J. Breinholt and T. V. Borchert, *Biorg. Med. Chem.*, 2000, **8**, 507.

7 A. Pulsipher, N. P. Westcott, W. Luo and M. N. Yousaf, *J. Am. Chem. Soc.*, 2009, **131**, 7626.

8 R. De Palma, S. Peeters, M. J. Van Bael, H. Van den Rul, K. Bonroy, W. Laureyn, J. Mullens, G. Borghs and G. Maes, *Chem. Mater.*, 2007, **19**, 1821.

9 D. Font, C. Jimeno and M. A. Pericàs, *Org. Lett.*, 2006, **8**, 4653.

10 D. Font, S. Sayalero, A. Bastero, C. Jimeno and M. A. Pericàs, *Org. Lett.*, 2008, **10**, 337.