Supplementary Information

S1. Experimental

S1.1. Materials and methods

2-Methoxy(polyethyleneoxy) propyltrimethoxysilane (Si-PEG, MW 1120-1250) was purchased from Gelest Inc. (Germany). 1,4,7-tris(tert-butoxycarboxymethyl)-1,4,7,10-tetraazadodecane (tBu-DO3A) was synthesised following literature methods, from cyclen purchased from CheMatech (France). All other chemicals were purchased from Sigma Aldrich, Acros or Alfa Aesar. External rare earth magnet (N42, NdFeB, 30 x 30 x 40 mm) was purchased from MagnetExpert Ltd. 1H NMR spectra were recorded on a Jeol JNM-LA400 spectrometer at 400 MHz in the solvent indicated, referenced against internal standard (TMS) or a residual non deuterated solvent signal. Mass spectrometry analyses were carried out on a Varian 500-MS LC-ion trap system. Transition Emission Microscopy (TEM) was performed by having suitable dilutions of samples dropped onto carbon-coated copper grids and allowed to air dry. Images were obtained using a Gatan US4000 digital camera (Gatan UK, Abingdon, Oxford) mounted onto a JEOL 2010 transmission electron microscope (Jeol UK) running at 200kV. FTIR spectra were collected using a Fourier transform infra-red spectrometer manufactured by Perkin Elmer (model Spectrum RXI). Nanoparticle tracking analysis (NTA) was carried out with a LM10-HS microscope from NanoSight® using a 75 mW laser at 532 nm (green). Zeta potential was measured with Zeta Nanosizer (Malvern Instruments, ZEN3600, UK) at 25°C, the conversion of the electrophoretic mobility (µ) into zeta potential (ζ) was performed using Smoluchowski equation. Gallium-68 was eluted from a 740 MBq 68Ge/68Ga generator (iThemba LABS/IDB Holland). Radio-TLC analyses were carried out using a Lablogic Scan-Ram, equipped with a NaI detector at a speed of 10mm/min. Data were recorded using Lablogic Laura (version 4.1.7.70) after developing silica plates (TLC-SG, Merck KGaA) in aqueous 0.1M citric acid solution.

S1.2. Synthesis of siloxane DO3A (1)

1,4,7-Tris(tert-butoxycarboxymethyl)-1,4,7,10-tetraazadodecane (tBu-DO3A) (1 g, 1.94 mmol) was dissolved in CHCl3 (4 ml), (3-glycidyloxypropyl)triethoxysilane (GPTES) (595 mg, 2.13 mmol) in CHCl3 (4 ml) was added dropwise and the reaction was heated by microwave irradiation at 90°C for 2 h then concentrated in vacuo. The crude oil was redissolved in CHCl3 (10 ml), washed with water (3 x 10 ml), dried (Na2SO4), filtered and concentrated in vacuo to yield an off white oil (1, 1.5 g, 97%). 1H-NMR (CDCl3): δ 0.57-0.64 (m, 2H, CH2), 1.18 (t, 9H, CH3), 1.41 (m, 27H, (CH3)3), 1.64-1.69 (m, 2H, CH2), 2.37-2.39 (m, 3H, CH2), 2.56-2.59 (m, 2H, CH2), 2.72-2.86 (m, 14H, CH2), 3.17-3.44 (m, 10H, CH2), 3.78 (q, 6H, CH2). MS (ESI): 793.8 [M+H]+.
S1.3. Synthesis and coating of nanorods

For synthesising the iron oxide nanorods the co-precipitation method was adopted following modified literature methods. In the presence of an external rare earth magnet, FeCl$_3$.6H$_2$O (10.9 g, 0.04 mol) and FeSO$_4$.7H$_2$O (6 g, 0.022 mol) were dissolved a mixture of 0.1 M HCl:ethanol (4:6, 1 L) and Ar was bubbled through during high speed stirring for 45 min before drop-wise addition of ammonium hydroxide (35%, 20 ml) over 15 min, during which a black precipitates formed. After the addition, the mixture was left stirring under argon for a further 30 min. The solid precipitate was attracted to the bottom of the flask using an external rare earth magnet and the clear aqueous layer was decanted. The washing and decanting procedure was repeated with 60% ethanol (2 x 500 ml), absolute ethanol (2 x 500 ml) and diethyl ether (500 ml) and the residue was finally dried under high vacuum to give NRs as a black powder (2, 6 g).

General procedure for coating nanorods with siloxanes: Freshly prepared nanorods (2) were coated with 1 and Si-PEG using a mixture of 1 and 2-[methoxy(polyethyleneoxy)-6-9proply]trimethoxysilane (Si-PEG) in different ratios. In each reaction, bare NRs (0.3 g, 1.3 mmol) were suspended under nitrogen in 60% ethanol (100 ml) by extensive sonication. Ammonium hydroxide (20 ml, 35%) was added drop-wise and the solution was stirred for 30 min. The designated amount of 1 and Si-PEG (total 0.086 mmol) dissolved in ethanol (10 ml) was added over 10 min and the reaction was stirred for 48 hours at room temperature. The solid precipitate formed was attracted to the bottom of the flask using an external rare earth magnet and the clear aqueous layer was decanted. The washing and decanting procedure was repeated with 60% ethanol (2 x 100 ml), ethanol (2 x 100 ml), methanol (2 x 100 ml) and diethyl ether (100 ml) and the residue was dried under high vacuum to give coated NRs as a black/brown powder. Amounts: Synthesis of 3 started with 1 (0.266 mg, 0.16 mmol) to give 0.223 g of 3. Synthesis of 4 started with 1 (0.133 g, 0.16 mmol) and Si-PEG (0.088 g, 0.16 mmol) to give 0.148 g of 4. Synthesis of 5 started with Si-PEG (0.176 g, 0.32 mmol) to give 0.190 g of 5.

Nanorods functionalised with 100% tBu-DO3A (3, 0.223 mg) or with 50% tBu-DO3A (4) (170 mg) were suspended in DCM (20 ml), TFA (2 ml) was added and the reaction was shaken at room temperature for 24 hours. The solid precipitate was attracted to the bottom of the flask using an external rare earth magnet and the clear aqueous layer was decanted. The washing and decanting procedure was repeated with ethanol (2 x 20 ml), methanol (20 ml) and diethyl ether (20 ml) and the residue was dried under high vacuum NRs as a black/brown powder (0.082 g and 0.170 g for 6 and 7, respectively).

S1.4. $^{68}$Ga preparation, radiolabelling and stability tests

Gallium-68 was obtained in the form of $^{68}$GaCl$_3$ from a commercial $^{68}$Ge/$^{68}$Ga generator. After elution of the generator with 3 ml of HCl 0.6 M (1 ml/min), the obtained eluate was diluted with ultra-pure water to reduce HCl concentration to 0.1 M and the $^{68}$Ga solution was then purified from $^{68}$Ge breakthrough by retention in a Strata-X-C 33µ polymeric strong cation exchange column (Phenomenex®) and further elution with 600 µl of acetone/HCl 0.05 M (98:2).
S2. FTIR

Figure S1. Overlaid FTIR spectra of 5-7.
S3. NTA

Figure S2. NTA of 5-7 before and after $^{68}$Ga radiolabelling.