Effective Am(III)/Eu(III) separations using BTP functionalised titania nanoparticles and beads

Jessica Veliscek-Carolan, Tracey L. Hanley, and Katrina A. Jolliffe

Table of Contents

Titania bead synthesis	
Organic ligand synthesis	S5
¹ H and ¹³ C NMR spectra of novel compound 1	
Sorption methodology	
XRD	S10
SAXS	S11
Protocol for covalent functionalization of titania	S12
Solid-state NMR	S12
CHN Microanalysis	S13
References	

Titania bead synthesis

Precursor solutions were prepared by addition of TiCl₄ to an ethanolic solution of triblock copolymer F127 (EO₁₀₀PO₇₀EO₁₀₀ where EO = ethylene oxide and PO = propylene oxide) in a glove box to exclude oxygen and water and allow efficient mixing of solutions prior to addition of water. After removal from the glove box, water was added to produce a clear, colourless solution which was sealed in a pyrex Schott bottle. The final molar ratio of TiCl₄ : ethanol : F127 : water was 1:40:0.01:10. Dissolution of the surfactant could not be completed until after the addition of water. The precursor solutions were aged statically at room temperature for 6 days before infiltration into polyacrylonitrile (PAN) beads.

Polyacrylonitrile (PAN) beads were generated using a 5 wt% PAN solution in DMSO and an automatic droplet generator at room temperature. To make the PAN solution, PAN (45 g) and DMSO (855 g) were mixed at 80 °C for 2 h then filtered through a 0.20 µm syringe filter. The automatic droplet generator was custom built with the capability to pass 500 mL of solution through the system in 3 min (Figure S1). A pyrex Schott bottle containing the PAN solution was placed in a CS-1560 Loctite pressure chamber, equipped with a pressure control knob. Pressure was generated from a HP-2.0, 2HDD air compressor. The PAN solution was passed into a specially designed PTFE nozzle (Figure S2) with three needle outlets. The needle tips were 21 gauge and were broken so as to be 1-4 mm in length. A Trio CS-1560 oscilloscope was used to measure the vibrations from the nozzle. The vibrations increased the regularity of the droplets. Droplets fell into a large beaker containing 4 L water and ~0.1 g Brij 58 ($C_{16}H_{33}EO_{20}$) to form solid beads and were stirred with an overhead paddle stirrer from Laboratory Supply P/L. The air compressor, the pressure chamber, and the nozzle were all connected with 13 mm Masterflex tubing. The beads were strained from the liquid then washed with distilled water until no surfactant foam was visible and the pH of the wash solution was that of distilled water, indicating that all of the Brij 58 had been removed.



Figure S1: Photograph and schematic of custom made automatic droplet generator.¹



Figure S2: Schematic drawings of PTFE nozzle of automatic droplet generator.¹

The PAN beads were placed in 160 mm petri dishes and underwent cross linking in a custom made 16 L evaporation chamber with controlled flow, temperature (37 °C) and humidity (50 % RH) for 3 days. The evaporation chamber was internally lined with low density polyethylene (LDPE) cling film and externally insulated using nitrile butadiene rubber (NBR)/PVC foam. The temperature in the evaporation chamber was controlled by flowing water through the walls of the chamber on a closed loop and a Polyscience temperature control unit was used to set the temperature of this water. The relative humidity and flow of air through the chamber were controlled using an IQI Instruquest HumiSys HF (High Flow) Relative Humidity Generator with a Watlow temperature control unit.

After humidification, the PAN beads were dried in air for 24 h then under vacuum for 3 h before addition of titania precursor solutions at a volume to mass ratio of 50. The PAN bead/precursor solution mixture was then degassed in a 3510E-DTH Bransonic Ultrasonic Cleaner at room temperature for 10 min and left to infiltrate for 24 h. Infiltration was evident when the PAN beads sank to the bottom of the precursor solution. After infiltration, the PAN beads were strained from the precursor solution and placed in 160 mm petri dishes lined with Whatman 42 filter paper to absorb any excess liquid. These petri dishes were then immediately placed in the custom evaporation chamber previously described and underwent evaporation induced self-assembly (EISA) at 37 °C and 50 % RH for 14 days. Temperature and relative humidity were measured periodically during evaporation using a calibrated Rotronic HygroPalm humidity probe.

After EISA, the titania beads were dried at 100 °C for 24 h. The template was then removed by heating at 200 °C for 2 h followed by 300 °C for 3 h and finally 350 °C for 12 h, with a ramp rate of 0.5 °C/min.

Organic ligand synthesis

The synthesis of the BTP derivative **h** described by Mercier et al. $(2010)^2$ was reproduced and is represented in Scheme S1.



Scheme S1: Synthesis of compound **h**. Conditions: (i) H_2SO_4 , EtOH, yield 82 %; (ii) K_2CO_3 , p-methoxybenzyl chloride, CH₃CN, yield 87 %; (iii) aqueous ammonia, MeOH, yield 64 %; (iv) pyridine, trifluoroacetic acid, CH₂Cl₂, yield 78 %; (v) hydrated hydrazine, EtOH, yield 86 %; (vi) 2,3-butanedione, Et₃N, THF, yield 89 %; (vii) Anisole, TFA, CH₂Cl₂, yield 84 %.

4-(11-undecen-1-yloxy)-2,6-bis(5,6-dimethyl-1,2,4-triazin-3-yl)pyridine (1):



1-Bromo-11-undecene (81 mg, 0.35 mmol) and potassium carbonate (0.24 g, 1.7 mmol) were added to a solution of 2,6-Bis(5,6-dimethyl-1,2,4-triazin-3-yl)-4hydroxypyridine (\mathbf{h} , 0.11 g, 0.34 mmol) in dimethylformamide (12 mL). The reaction mixture was stirred under reflux for 4 h. The solvent was then removed under reduced pressure and the resulting dark green solid resuspended in CH₂Cl₂ before filtration. The residue was rinsed with CH₂Cl₂ (approx. 10 mL) and the filtrate then removed under reduced pressure to afford the crude product as a dark green oil. Purification by flash chromatography (CH₂Cl₂ then 98:2 CH₂Cl₂:methanol) afforded the pure product as a yellow oil (46 mg, 29 % yield). HRMS (ESI) calcd for C₂₆H₃₅N₇O [M+Na]⁺ m/z484.2801, found 484.2796. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.33 (s, 2H), 5.81 (m, 1H), 4.97 (m, 2H), 4.25 (t, J = 6.6 Hz, 2H), 2.79 (s, 6H), 2.71 (s, 6H), 2.05 (dt, J =7.2, 6.8 Hz, 2H), 1.89 (tt, J = 7.4, 6.6 Hz, 2H), 1.50 (m, 2H), 1.45-1.20 (m, 10H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 167.3, 161.3, 159.7, 157.2, 154.9, 139.2, 114.1, 111.9, 68.8, 33.8, 29.5, 29.4, 29.3, 29.1, 28.9, 25.9, 21.9, 19.7. FTIR (ATR, neat): v_{max} 3362, 3074, 2922, 2851, 1675, 1640, 1591, 1571, 1535, 1426, 1388, 1359, 1333, 1308, 1240, 1194, 1161, 1128, 1091, 1033, 1010, 991, 976, 905, 872, 831, 796, 735 cm⁻¹.

¹H and ¹³C NMR spectra of novel compound 1



S7



Sorption methodology

To prepare 10 ppb ²⁴¹Am solutions, 28 μ L aliquots of a ²⁴¹Am stock solution (2.1 MBq/mL, 3 M nitric acid, specific activity ²⁴¹Am = 118.4 MBq/mg) were diluted to 50 mL with either 0.1 M (pH 1) or 0.01 M (pH 2) nitric acid. To prepare the 10 ppb Eu solutions, a 3.6 mL spike of ¹⁵²Eu stock solution (1.0 kBq/mL, specific activity ¹⁵²Eu = 6.7 GBq/mg) and 20 μ L of 10 ppm carrier Eu were diluted to 20 mL with 0.01-0.1 M nitric acid. Individual element sorption and kinetics experiments were performed in duplicate with pH 1-2 ²⁴¹Am or spiked ¹⁵²Eu solutions, either fully

aqueous or containing 10 % ethanol. All sorption experiments were performed via the batch contact method and using a constant volume-to-mass ratio of 200 mL/g. The solutions and powders or beads were contacted in plastic screw-cap vials. Samples were shaken on a vertical mixer at a constant speed of approximately 10 rpm for a period of 24 h (or for designated time for kinetic measurements). After sorption, nanoparticle suspensions were filtered through individual 0.45 μ m syringe filters while the liquid from the bead suspensions was decanted off using a glass pipette.

The resulting liquids from both nanoparticle and bead sorption experiments were analysed by gamma counting each duplicate sample for 1 h. Initial concentrations before sorption were measured from samples shaken and filtered as described above but in the absence of any sorbent material (as a control), to ensure that metal sorption to the plastic vial or filter did not affect the reported results. Measurements of the controls were the same as the concentrations measured of the original solutions that were not shaken and filtered. Partition coefficients (D) were calculated by measuring the activity of the analyte before and after sorption by gamma counting.

$$D = [(A_f - A_i)/A_f]^*(V/m)$$

Where A_f is the final activity of the analyte after sorption (cpm), A_i is the initial activity before sorption (cpm), V is the volume of solution added during the adsorption experiment (mL) and m is the mass of sorbent material used (g). Errors in the reported partition coefficient (D) values were calculated from the standard deviation of the gamma counting results. If the standard deviation was less than 1 % of the measured D value, an error of 1 % was applied. The partition coefficients (mL/g) of particular analytes were then used to calculate separation factors:

Separation Factor $(SF_{A/B}) = D_A/D_B$ *XRD*



Figure S5: XRD pattern of titania beads

SAXS



Figure S6: SAXS patterns of titania beads during thermal treatment

After drying at 100 °C, the titania beads had d-spacing 14 nm, full-width halfmaximum (FWHM) 0.01 and relative intensity 2. After thermal treatment at 300 °C for 3 h, the titania beads had d-spacing 10 nm, FWHM 0.01 and relative intensity 4. After 12 h at 350 °C, which was required to remove the PAN and F127 polymer templates, the titania beads had d-spacing 9 nm, FWHM 0.01 and relative intensity 2. The SAXS data of the titania beads after template removal at 350 °C for 12 h was also fit using SASView software with two power laws and a Lorentzian peak, in order to more accurately model the data. A power law of exponent -2.5 was fit from Q = 0.02 to 0.05 Å⁻¹ followed by a power law exponent of -3.8 from Q = 0.05 to 0.39 Å⁻¹ and the Lorentzian peak had d-spacing 100 ± 10 Å, half-width-half-maximum 0.009 ± 0.00002 Å⁻¹ and scale 8931 ± 15. The fitted data is shown as a solid line in Figure S4 and can be seen to provide a good fit to the experimental data (χ^2 /Npts = 84). The presence of a two different power law exponents at different Q ranges indicates that there are different morphologies present at different length scales, which is to be expected for a hierarchically porous material such as this.

Protocol for covalent functionalization of titania

Dry titania particles or beads were mixed with a dry, degassed solution of compound **1** and 1-undecene in mesitylene (0.11 M) under nitrogen. The resulting suspension was heated in an oil bath at 115 °C for 24 h, with stirring, then filtered. The residue was washed with petroleum ether (5 mL), methanol (5 mL) and CH_2Cl_2 (5 mL) before drying under vacuum, affording the functionalised particles or beads.

Solid-state NMR



Figure S7: ¹³C-¹H CP MAS NMR spectra of P-alkene, P-BTP4 and TB-BTP

The presence of peaks in the solid-state ${}^{13}C{}^{-1}H$ CP MAS NMR spectra of P-alkene and P-BTP4 (Figure S7) confirms that functionalization was successful. Peaks with chemical shift 15-45 ppm, due to aliphatic CH₂ groups,³ are seen in the NMR spectra of both P-alkene and P-BTP4 as both the 1-undecene and Me-BTP-Oundecene ligands used for functionalisation contain alkyl chains. Since this is the only carbon containing functionality present in P-alkene, no other peaks are seen in its NMR spectrum. However, the NMR spectra of P-BTP4 and TB-BTP also show a peak with a chemical shift of approximately 65-75 ppm which can be assigned as the CH₂-O moiety in the Me-BTP-O-undecene ligand.³ Therefore the ${}^{13}C{}^{-1}H$ CP MAS NMR spectra also confirm the presence of the Me-BTP-O-undecene ligand on the surface of P-BTP4 and TB-BTP.

CHN Microanalysis

CHN analysis was performed by the Microanalytical Unit at the Macquarie University using an Elemental Analyser, Model PE2400 CHNS/O (PerkinElmer, Shelton, CT, USA) with PC based data system, PE Datamanager 2400 for WindowsTM and a PerkinElmer AD-6 Ultra Micro Balance. The sample is combusted, and the combustion products passed over catalysts and oxidisation reagents to form CO_2 , H_2O and N_2 from the elemental C, H and N, respectively. The amount of CO_2 , H_2O and N_2 is then measured using frontal gas chromatography.

The level of functionalization of titania nanoparticles (P-BTP4) and beads was quantitatively determined by CHN microanalysis (Table S1). It was assumed that for every molecule of **1** ($C_{26}H_{35}N_7O$) present there was 4 molecules of 1-undecene ($C_{11}H_{22}$) also present, so that the overall molecular formula of the organic functional groups was $C_{70}H_{123}N_7O$. The molecular formulae of the organic functionalised molecules and the total measured %CHN were used to determine the calculated %CHN values, which agreed with the experimentally measured values to within 0.2 %. The total organic contents of the organo-functionalised titania nanoparticles and beads was then calculated as the percentage weight of CHNO. CHN analysis was not performed for P-BTP2 and P-BTP8 because with a total organic content of 1.7 %, the difference in the percentage of C, H and N would be less than 0.1 % for the different ratios of compound **1** : 1-undecene and hence would be undetectable.

Measured	P-BTP4	TB-BTP
%C	1.1	2.6
%Н	0.3	0.5
%N	0.3	0.2
Total	1.7	3.3
Calculated	C ₇₀ H ₁₂₃ N ₇ O	C70H123N7O
%C	1.3	2.6
%Н	0.2	0.4
%N	0.2	0.3
Total (organic)	1.7	3.4

Table S1: Elemental CHN microanalysis of functionalised titania nanoparticles (P-BTP4) and beads (TB-BTP) (weight %)

References

- 1 G. L. Drisko, M. C. Kimling, N. Scales, A. Ide, E. Sizgek, R. A. Caruso and V. Luca, *Langmuir*, 2010, **26**, 17581.
- 2 D. Mercier, N. Leconte, C. Methivier, F. Suzenet, G. Guillaumet, A. Wuillaume and C. M. Pradier, *Phys Chem Chem Phys*, 2010, **12**, 6099.
- 3 E. V. Breitmaier, W., Carbon-13 NMR Spectroscopy High Resolution Methods and Applications in Organic Chemistry and Biochemistry, VCH, Weinheim, 1987.