

A Highly Efficient Solvent System Containing Functionalized Diglycolamides and an Ionic Liquid for Americium Recovery from Radioactive Wastes

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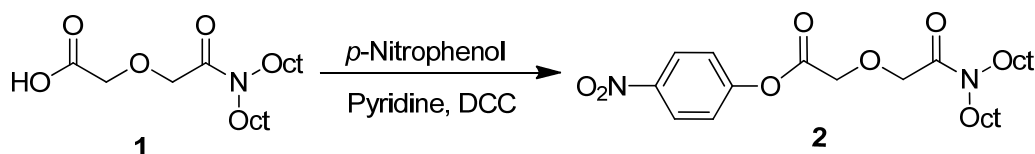
Supplementary Information

Experimental Section

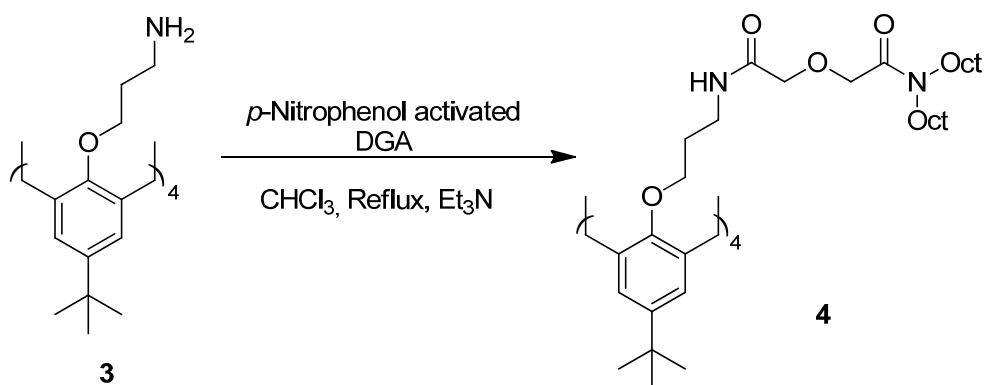
General. All moisture-sensitive reactions were carried out under an argon atmosphere. The solvents and all reagents were obtained from commercial sources and used without further purification. All known compounds *viz.* **1**¹, **3**², **5**³, and **7**⁴ were prepared according to literature procedures. Solvents were dried according to standard procedures and stored over molecular sieves. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Unity INOVA (300 MHz) spectrometer. ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) chemical shift values are reported as δ using the residual solvent signal as an internal standard. All NMR measurements are recorded in CDCl₃ as a solvent. Electrospray Ionization (positive mode) mass spectra and high resolution mass spectra were recorded on a WATERS LCT mass spectrometer. Analytical TLC was performed using Merck prepared plates (silica gel 60 F-254 on aluminum). Column chromatography was carried out with Merck silica gel 60 (230–400 mesh).

***p*-Nitrophenol activated DGA (2).** A solution of *N,N*-dioctylglycolic acid (**1**) (2.00 g, 5.6 mmol), *p*-nitrophenol (0.81 g, 5.7 mmol), and DCC (1.22 g, 5.8 mmol) in pyridine (60 mL) was stirred overnight at room temperature. The solvent was evaporated and the residue was dissolved in *n*-hexane, filtered and the filtrate was washed with 4% NaHCO₃ solution (2 x 50 mL). The organic layer was dried with anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (CH₂Cl₂:MeOH, 98:2) to afford *p*-nitrophenol activated DGA (**2**) (2.16 g, 81%) as a light yellow oil. ¹H NMR: δ 0.81-0.93 (m, 6H, CH₃), 1.14-1.38 (m, 20H, CH₃(CH₂)₅), 1.45-1.60 (m, 4H, NCH₂CH₂), 3.18 and 3.31 (t, 2H $J = 7.5$ Hz, NCH₂), 4.37 (s, 2H, OCH₂), 4.58 (s, 2H, OCH₂), 7.33 (d, 2H, $J = 9.0$

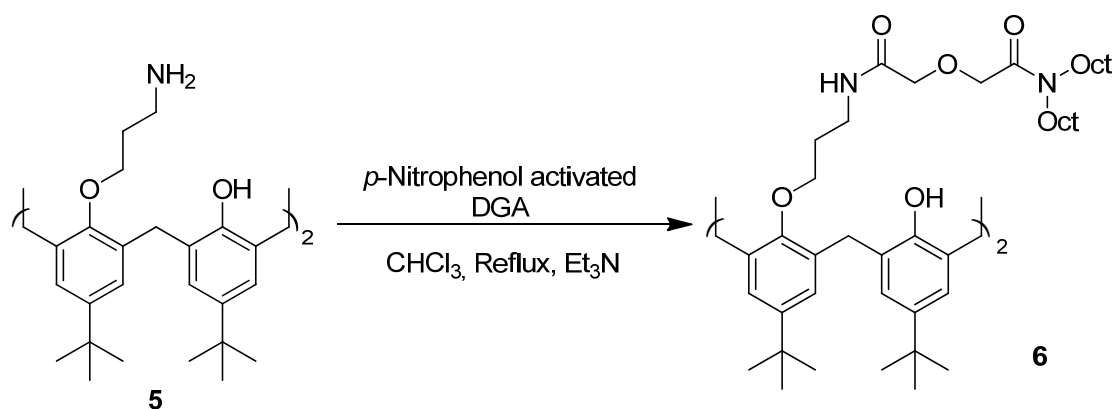
Hz, ArH), 8.28 (d, 2H, $J = 9.0$ Hz, ArH); ^{13}C NMR: δ 14.3, 22.8, 29.5, 31.9, 60.1, 68.2, 69.4, 122.5, 125.5, 126.3, 145.9, 169.1; HRMS: m/z 479.3130 ($\text{M}+\text{H}$) $^+$, calculated: 479.3121.



Calix[4]arene 4-DGA (4). A mixture of **3** (0.45 g, 0.5 mmol), *p*-nitrophenol activated DGA (**2**) (1.20 g, 2.5 mmol) and triethylamine (0.25 g, 2.5 mmol) in chloroform (50 mL) was refluxed overnight. The crude reaction mixture was successively washed with 2M NaOH solution (3 x 50 mL), 1M HCl (3 x 50 mL), and water (2 x 50 mL). The organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography (CH_2Cl_2 :MeOH, 96:4) to afford calix[4]arene 4-DGA (**4**) (1.10 g, 71%) as a dense oil. ^1H NMR: δ 0.81-0.93 (m, 24H, CH_3), 1.07 (s, 36H, *t*-Bu), 1.17-1.35 (m, 80H, $\text{CH}_3(\text{CH}_2)_5$), 1.43-1.60 (m, 16H, NCH_2CH_2), 2.25 (pentet, 8H, $J = 6.0$ Hz, OCH_2CH_2), 3.04-3.16 (m, 12H, ArCH_2Ar and NCH_2), 3.27 (t, 8H, $J = 7.5$ Hz, NCH_2), 3.46 (t, 8H, $J = 6.0$ Hz, NHCH_2), 3.89 (t, 8H, $J = 6.0$ Hz, ArOCH_2), 4.09 (s, 8H, OCH_2CO), 4.27 (s, 8H, OCH_2CO), 4.34 (d, 4H, $J = 12.0$ Hz, ArCH_2Ar), 6.75 (s, 8H, ArH), 7.97-8.07 (m, 4H, NH); ^{13}C NMR: δ 14.3, 22.9, 27.1, 29.5, 31.6, 32.0, 34.0, 36.7, 46.3, 47.0, 60.1, 133.9, 144.8, 153.5, 168.4, 170.0; MS: m/z 2234.7 ($\text{M}+\text{H}$) $^+$, calculated: 2234.8.



Calix[4]arene 2-DGA (6) was prepared in an analogous way as **4** starting from **5** (1.60 g, 2.1 mmol) and *p*-nitrophenol activated DGA (**2**) (2.11 g, 4.4 mmol) in the presence of triethylamine (0.46 g, 4.5 mmol), and purified by column chromatography (CH₂Cl₂:MeOH, 96:4) in 77% yield (2.20 g) as a dense oil. ¹H NMR: δ 0.83-0.93 (m, 12H, CH₃), 0.99 (s, 18H, *t*-Bu), 1.18-1.38 (m, 58H, *t*-Bu and CH₃(CH₂)₅), 1.42-1.57 (m, 8H, NCH₂CH₂), 2.26 (pentet, 4H, *J* = 6.0 Hz, OCH₂CH₂), 3.03 (t, 4H, *J* = 7.5 Hz, NCH₂), 3.21-3.33 (m, 8H, ArCH₂Ar and NCH₂), 3.74 (t, 4H, *J* = 6.0 Hz, NHCH₂), 4.05 (t, 4H, *J* = 6.0 Hz, ArOCH₂), 4.11 (s, 4H, OCH₂CO), 4.16 (s, 4H, OCH₂CO), 4.25 (d, 4H, *J* = 12.0 Hz, ArCH₂Ar), 6.83 (s, 4H, ArH), 7.02 (s, 4H, ArH), 7.68 (s, 2H, ArOH), 8.09-8.18 (m, 2H, NH); ¹³C NMR: δ 14.3, 22.9, 27.3, 29.5, 31.3, 32.0, 34.1, 34.2, 69.7, 71.7, 125.7, 127.9, 132.9, 141.8, 147.2, 149.7, 150.7, 168.6, 170.4; HRMS: *m/z* 1441.0741 (M+H)⁺, calculated: 1441.0882.

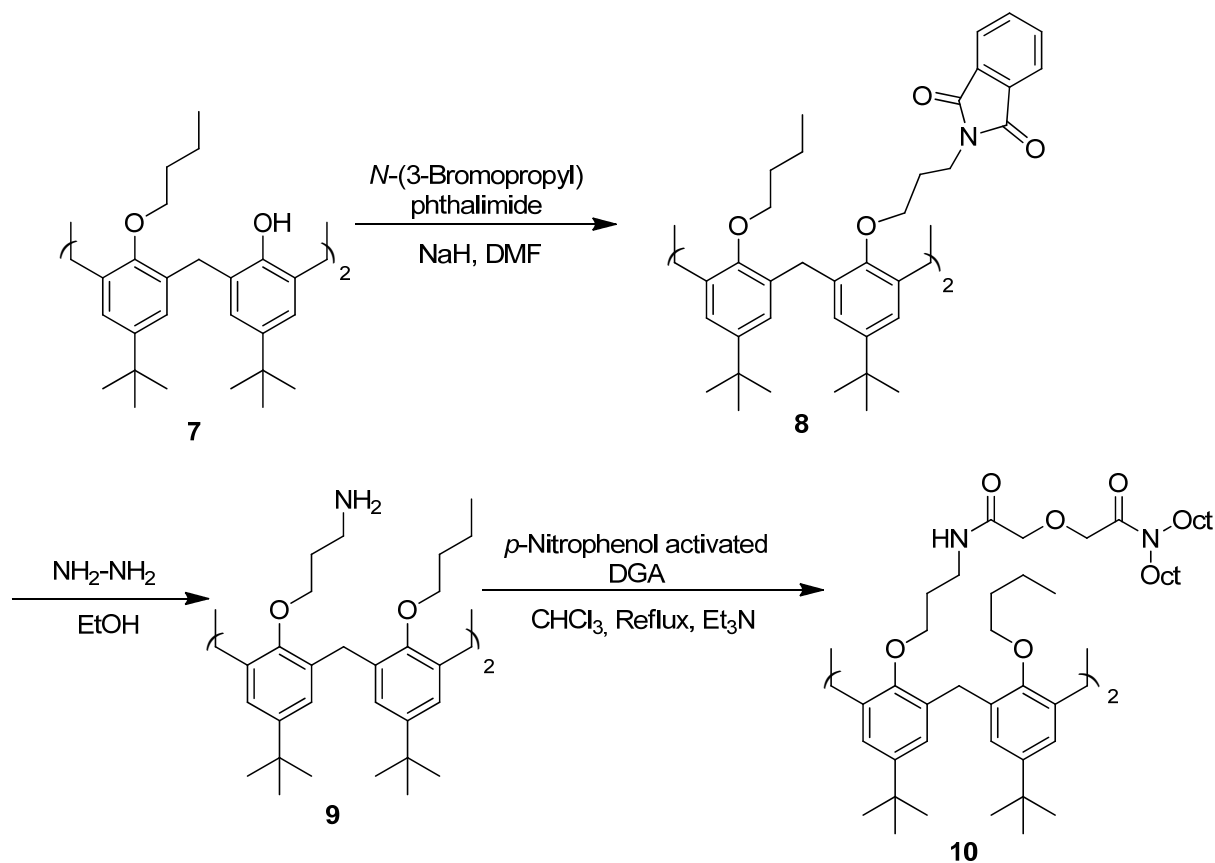


1,3-Dibutoxy-2,4-bis(phthalimidopropoxy)calix[4]arene (8). A suspension of **7** (2.50 g, 3.3 mmol) in DMF (60 mL) was stirred under argon for 30 min. NaH (60% in oil, 1.00 g, 26.2 mmol) was added and stirring was continued for 1 h. *N*-(3-Bromopropyl) phthalimide (3.51 g, 13.1 mmol) was then added and the mixture was stirred for 3 d at room temperature. After addition of water (100 mL) the resulting precipitate was collected, dissolved in chloroform

(100 mL) and washed with 15% HCl (50 mL). Evaporation of the solvent, after drying (MgSO₄), followed by precipitation from chloroform–methanol gave the target product **8** (2.46 g, 66%) as a white solid. M.p. 108-110 °C; ¹H NMR: δ 0.92 (s, 18H, *t*-Bu), 0.99 (t, 6H, *J* = 7.5 Hz, CH₃), 1.21 (s, 18H, *t*-Bu), 1.43 (sextet, 4H, *J* = 7.5 Hz, CH₃CH₂(Bu)), 1.86 (pentet, 4H, *J* = 7.5 Hz, OCH₂CH₂(Bu)), 2.52 (pentet, 4H, *J* = 7.5 Hz, OCH₂CH₂(PrPhth)), 3.10 (d, 4H, *J* = 12 Hz, ArCH₂Ar), 3.75 (t, 4H, *J* = 7.5 Hz, CH₂Phth), 3.89 (t, 4H, *J* = 7.5 Hz, OCH₂(Bu)), 4.07 (t, 4H, *J* = 7.5 Hz, OCH₂(PrPhth)), 4.36 (d, 4H, *J* = 12 Hz, ArCH₂Ar), 6.57 (s, 4H, ArH), 6.93 (s, 4H, ArH), 7.66-7.71 (m, 2H, ArPhth), 7.79-7.86 (m, 2H, ArPhth); ¹³C NMR: δ 14.2, 19.5, 29.9, 31.3, 31.5, 31.9, 32.5, 33.9, 34.2, 81.8, 103.1, 123.4, 125.1, 129.4, 132.5, 132.9, 135.0, 144.2, 144.9, 153.2, 154.3, 168.5; HRMS: *m/z* 1135.6779 (M+H)⁺, calculated: 1135.6775.

1,3-Dibutoxy-2,4-bis(aminopropyl)calix[4]arene (9). Hydrazine hydrate (10 mL, 200 mmol) was added to a suspension of **8** (2.00 g, 1.7 mmol) in ethanol (50 mL). The mixture was refluxed for 12 h, cooled and then diluted with water (100 mL). A precipitate formed which was extracted into dichloromethane (4 × 50 mL). The organic layer was then dried (MgSO₄) and the solvent was evaporated to give **9** (1.51 g, 98%) as a white solid. M.p. 73-75 °C; ¹H NMR: δ 0.98-1.02 (m, 24H, (CH₃ and *t*-Bu)), 1.16 (s, 18H, *t*-Bu), 1.41 (sextet, 4H, *J* = 7.5 Hz, CH₃CH₂(Bu)), 1.93 (pentet, 4H, *J* = 7.5 Hz, OCH₂CH₂(Bu)), 2.18 (pentet, 4H, *J* = 7.5 Hz, OCH₂CH₂(PrNH₂)), 3.10 (t, 4H, *J* = 7.5 Hz, CH₂NH₂), 3.16 (d, 4H, *J* = 12 Hz, ArCH₂Ar), 3.93 (t, 4H, *J* = 7.5 Hz, OCH₂(Bu)), 4.02 (t, 4H, *J* = 7.5 Hz, OCH₂(PrNH₂)), 4.37 (d, 4H, *J* = 12 Hz, ArCH₂Ar), 6.74 (s, 4H, ArH), 6.91 (s, 4H, ArH); ¹³C NMR: δ 14.5, 19.5, 29.9, 31.6, 32.4, 34.1, 39.1, 60.1, 73.0, 76.8, 125.4, 133.7, 134.3, 144.5, 144.9, 152.9, 153.6; HRMS: *m/z* 875.6639 (M+H)⁺, calculated: 875.6666.

1,3-Dibutoxycalix[4]arene 2-DGA (10) was prepared in an analogous way as **4** starting from **9** (1.05 g, 1.2 mmol) and *p*-nitrophenol activated DGA (**2**) (1.40 g, 2.8 mmol) in the presence of triethylamine (0.30 g, 2.8 mmol), and purified by column chromatography (CHCl₃:MeOH, 97:3) in 64% yield (1.20 g) as a dense oil. ¹H NMR: δ 0.83-0.93 (m, 12H, CH₃), 0.99 (t, 6H, *J* = 7.5 Hz, (CH₃(Bu))), 1.07 (s, 18H, *t*-Bu), 1.08 (s, 18H, *t*-Bu), 1.20-1.35 (m, 40H, CH₃(CH₂)₅), 1.42 (sextet, 4H, *J* = 7.5 Hz, CH₃CH₂(Bu)), 1.45-1.60 (m, 8H, NCH₂CH₂), 1.97 (pentet, 4H, *J* = 7.5 Hz, OCH₂CH₂(Bu)), 2.26 (pentet, 4H, *J* = 7.5 Hz, OCH₂CH₂), 3.04-3.18 (m, 8H, NCH₂ and ArCH₂Ar), 3.28 (t, 4H, *J* = 7.5 Hz, NCH₂), 3.49 (t, 4H, *J* = 7.5 Hz, NHCH₂), 3.89 (pentet, 8H, *J* = 7.5 Hz, ArOCH₂), 4.08 (s, 4H, OCH₂CO), 4.24 (s, 4H, OCH₂CO), 4.38 (d, 4H, *J* = 12.0 Hz, ArCH₂Ar), 6.75 (s, 4H, ArH), 6.77 (s, 4H, ArH), 7.75-7.83 (m, 2H, NH); ¹³C NMR: δ 14.4, 19.6, 23.0, 27.1, 29.5, 31.6, 32.1, 34.0, 69.8, 72.1, 81.8, 103.2, 125.1, 134.0, 144.5, 153.6, 168.3, 169.7; HRMS: *m/z* 1554.2200 (M+H)⁺, calculated: 1554.2213.



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