Separation of Am(III), Cm(III) and Eu(III) by electro-spun polystyrene-immobilized CyMe$_4$-BTPhen

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ABSTRACT

The synthesis of a novel 5-(4-vinylphenyl)-CyMe$_4$-BTPhen actinide selective ligand using selenium free synthetic procedures is reported. For the first time, we report the electrospinning of this actinide selective ligand into a polystyrene fiber and investigate its selective removal of Am(III) from Eu(III) and Am(III) from Cm(III). At 4 M HNO$_3$, the resulting fibrous solid extractant produced separation factors of $SF_{Am/Eu} \approx 57$ and a small, but significant separation of $SF_{Am/Cm} \approx 2.9$.

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1. Introduction

The generation of used nuclear fuel (commonly known as "spent nuclear fuel", SNF) has contributed to the global accumulation of actinides, where the separation of these radiotoxic elements is strongly affected by the presence of other elements, including transition metals and lanthanides, which compete for the binding sites in the ligands used for their separation [1–3]. After the removal of uranium (U) and plutonium (Pu) from the SNF by the currently employed PUREX process, most of the long-term radiotoxicity and heat-load of the waste arises from the presence of the minor actinides (americium, curium and neptunium), even though they only account for a small proportion of the waste (~0.1%) [4]. Selective separation of the actinides Am(III) and Cm(III) from fission products and closely related lanthanides has been previously achieved using soft *N*-donor ligands such as (**1**), (**2**) and (**3**), which contain the 1,2,4-triazine moiety (Fig. 1) [5–10].

It is generally accepted that one of the contributors to this selectivity is due to the more radially expanded nature of the 5*f*-obitals of the actinides compared to the 4*f*-orbitals of the lanthanides [11–13]. It is rationalized that this subtle difference means that soft *N*-donor extractants have increased ligand-actinide bond covalency and hence selectivity over the lanthanides. More recently, substitution at different positions of the 1,10-phenanthroline core in (**3**) has provided the ability to fine-tune the ligands electronically to be even more selective towards actinides over lanthanides. The efficiency for the extraction of the actinides over lanthanides by some di-amide and calixarene-based extractants has also been reported [14–16]. Furthermore, electronically modulated Br-CyMe$_4$-BTPhen (**4**) and 5-(4-hydroxyphenyl)-CyMe$_4$-BTPhen (**5**) (Fig. 2) have been shown to exhibit slight, but significant selectivity for Am(III) over Cm(III), elements that are adjacent to each other in the periodic table [17].

The ligands shown in Fig. 2 provide a means of amplifying the very small differences in the covalent interactions of Am(III) and Cm(III) with the ligands by subtle electronic modulation with 5-bromo- (**4**) and 5-(4-hydrxyphenyl)- (**5**) substituents, revealing separation factors for Am(III) over Cm(III) ($SF_{Am/Cm}$) as high as 7 [18,19].

There are several partitioning processes that have been proposed and studied to separate Am(III) from Eu(III), but most of these processes focus entirely on solvent extraction processes which possess certain disadvantages, including the need for large

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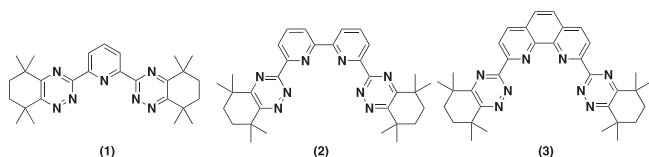
Fig. 1. Structures of CyMe$_4$-BTP (**1**), CyMe$_4$-BTBP (**2**) and CyMe$_4$-BTPhen (**3**).
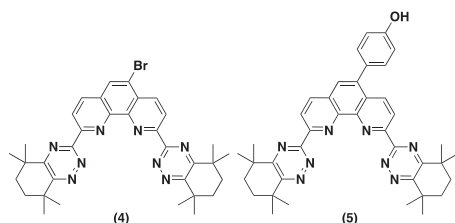
Fig. 2. Structures of Br-CyMe$_4$-BTPhen (**4**) and 5-(4-hydroxyphenyl)-CyMe$_4$-BTPhen (**5**).
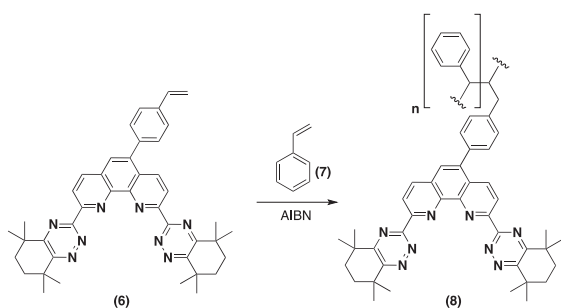
volumes of organic solvents and degradation of the solvents over time, resulting in reduced performance and efficiency. Often these liquid-liquid extraction systems require the use of phase modifiers to optimize extraction and third phase formation can be encountered. Extraction systems based on immobilized extractants would remove the need for excessive organic solvents. Synthesis of ligand (**5**) enabled immobilization of CyMe$_4$-BTPhen ligands onto solid supports, notably magnetic nano-particles (MNPs) and macroscopic silica gel, where their ability to separate Am(III) from Eu(III) has been previously demonstrated [20,21]. Related materials have also been prepared by cross-linking Me$_4$-BTPhen into PVB (poly-vinyl benzyl) polymers and its Am(III) extraction ability was investigated [22]. The ability of these solid supports to be implemented in the extraction of Am(III) from Eu(III) in solutions of up to 4 M HNO$_3$ has opened up an area of research geared towards functionalizing solid materials for selective actinide separation. Moving towards solid supported processes, and in particular using column separation techniques, may ultimately help reduce the solvent waste generated by continuous solvent extraction processes.

In this work, we outline the synthesis of novel 5-(4-vinylphenyl)-CyMe$_4$-BTPhen (**6**) using a selenium-free synthetic protocol and report the ability of this ligand to separate Am(III) from Eu(III) and Am(III) from Cm(III) when immobilized into fibers of electro-spun polystyrene (**8**) (Scheme 1).

2. Results and discussion

2.1. Synthesis of 5-(4-vinylphenyl)-CyMe$_4$-BTPhen (**6**)

Until recently, the synthesis of the core CyMe$_4$-BTPhen (**3**) unit

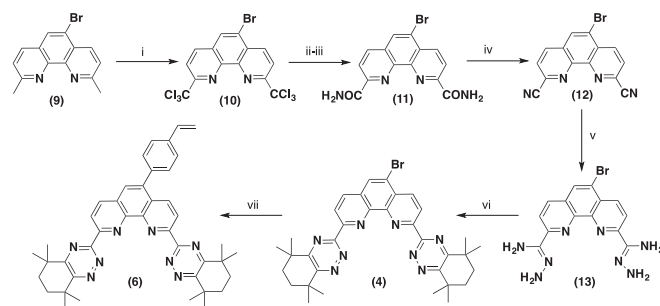**Scheme 1.** Synthesis of polystyrene immobilized CyMe$_4$-BTPhen (**8**).

required the use of stoichiometric amounts of toxic selenium dioxide to generate the phenanthroline *bis*-aldehyde, required for the one-pot conversion to the phenanthroline *bis*-nitrile, where nitrile functional groups are key precursors to produce many heterocyclic cores [23]. Edwards et al. demonstrated that the benzylic oxidation could be achieved by per-chlorination of the methyl groups in 2,9-dimethyl-1,10-phenanthroline and subsequent hydrolysis/methyl-ation to give a *bis*-ester [19,24]. Conversion to a *bis*-amide and dehydration afforded the *bis*-nitrile compound required to develop BTPhen (**3**) related ligands [21]. In an alternative approach, the installation of nitrile groups into 1,10-phenanthroline derivatives has been achieved using photochemical reactions, where C–H functionalization of substituted phenanthroline units using a transient α-amido radical afforded phenanthroline *bis*-amides, which were then dehydrated to the corresponding *bis*-nitriles by *in situ* preparation of Vilsmeier-Haack reagent [25]. Following these developments in the synthesis of BTPhen ligands, Br-CyMe$_4$-BTPhen (**4**) was synthesized using the improved synthetic protocol (Scheme 2) [19,21]. Suzuki-Miyaura cross coupling with 4-vinylphenyl boronic acid afforded the novel 5-(4-vinylphenyl)-CyMe$_4$-BTPhen (**6**) required for bulk polymerization with styrene [26].

Polystyrene units can be polymerized in bulk at temperatures of >100 °C without the need for the addition of an initiator, where control of the polymers molecular weight is lost. More controlled polymerization can take occur at lower temperatures (ca. 55–60 °C), with the addition of initiators, typically benzoyl peroxide or AIBN (azo-*bis*-isobutyronitrile) [27]. 5-(4-Vinylphenyl)-CyMe$_4$-BTPhen (**6**) was subsequently co-polymerized with styrene using AIBN as the initiator (Scheme 1). Electrospinning the 5-(4-vinylphenyl)-CyMe$_4$-BTPhen-styrene co-polymer (**8**) produced fine pale yellow fibers, resembling cotton-wool.

2.2. Characterization of electro-spun fibers (**8**)

The polystyrene-immobilized CyMe$_4$-BTPhen fibers (**8**) were characterized to assess the immobilization of the ligand and to investigate structural features using Fourier-transform infrared spectroscopy (FT-IR), elemental analysis (ESI) and scanning electron microscopy (SEM) (Fig. 3).

The SEM images at different magnifications clearly show the regularity in diameter and high surface area of these fine fibers and elemental analysis reveals the incorporation of nitrogen into the co-polymer (ESI). The FT-IR spectrum of the electro-spun polystyrene-immobilized CyMe$_4$-BTPhen fibers (**8**) shows overlapping bands due to aromatic C–C stretching of the styrene residues, and additional aromatic vibrations for the ligand (ESI). The GPC (gel permeation chromatography) eluogram of electro-spun polystyrene immobilized CyMe$_4$-BTPhen fibers (**8**) is shown below in

Scheme 2. Synthesis of 5-(4-vinylphenyl)-CyMe$_4$-BTPhen (6): i) NCS, *m*-CPBA, CHCl$_3$, 90%; ii) H$_2$SO$_4$ then MeOH, 70%; iii) NH$_4$Cl, NH$_4$OH, 89%; iv) POCl$_3$, 90%; v) N$_2$H$_4$·H$_2$O (64%), DMSO, 60%; vi) 3,3,6,6-tetramethylcyclohexan-1,2-dione, THF, Et$_3$N, 55%; vii) 4-vinylboronic acid, Pd(PPh$_3$)$_4$, K$_2$CO$_3$, PhMe:EtOH:H$_2$O (5:1:1), 50%.
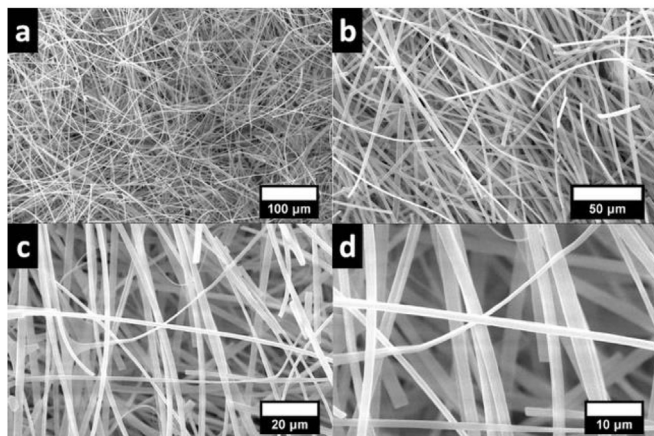
Fig. 3. SEM images of polystyrene-immobilized CyMe$_4$-BTPhen fibers (**8**). Horizontal axis scale: a) 500 µm b) 200 µm c) 20 µm d) 2.0 µm.
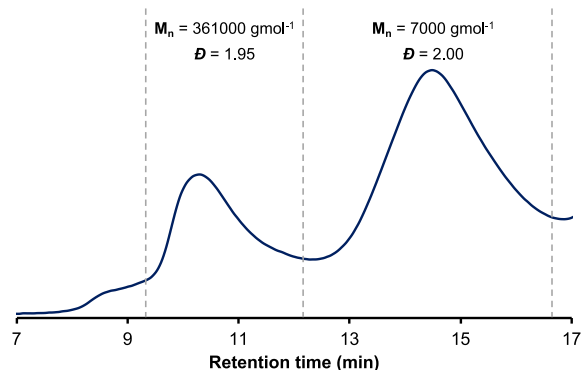

Fig. 4. GPC eluogram of polystyrene-immobilized CyMe$_4$-BTPhen fibers (**8**).

Fig. 4. Not untypically for materials produced this way, the material had a broad molecular weight distribution, consisting of a high molecular weight component and a low molecular fraction; the overall distribution values revealed for M_n were 361.0 and 7.0 kg mol^{-1} respectively with dispersion values (Đ) of 1.95 and 2.00 respectively. This higher weight component presumably facilitates the entanglements necessary for electrospinning [28].

2.3. Extraction data

The ability for polystyrene immobilized CyMe$_4$-BTPhen (**8**) to extract Am(III), Cm(III) and Eu(III) across a range of HNO$_3$ concentration was investigated (see Table 1). The extraction results for Am(III)/Eu(III) by (**8**) showed good distribution ratios for both Am(III) ($D_{wAm} = 490 \pm 24$ mL/g) and Eu(III) ($D_{wEu} = 66 \pm 1$ mL/g) at 0.001 M HNO$_3$ with a separation factor of $SF_{Am/Eu} = 7.40 \pm 0.24$ (Table 2). However, these values are much lower than those

Table 1
Extraction of Am(III) and Eu(III) by (**8**) as a function of nitric acid concentration. Mass of sorbent: accurately approximately 19.8 mg, phase volume: 1.0 mL, *V/m* ratio: ~30.3 mL/g.

c(HNO$_3$)	D_w(Am)			D_w(Eu)			SF(Am/Eu)		
0.001	490	±	24	66	±	1	7.40	±	0.24
0.1	781	±	46	20	±	1	39.1	±	1.5
1	387	±	17	7.7	±	0.2	50	±	2
4	188	±	7	3.3	±	0.4	57.1	±	4.1

obtained for the same CyMe4-BTPhen unit covalently bound to SiO2-coated MNPs ($D_{Am} = 1168.8 \pm 79.1$ mL/g and $D_{Eu} = 701.4 \pm 32.4$ mL/g) [29]. Increasing the HNO$_3$ concentration led to an increase in Am(III) extraction ($D_{wAm} = 781 \pm 46$ mL/g), and a decrease in Eu(III) extraction ($D_{wEu} = 20 \pm 1$ mL/g) giving a separation factor of $SF_{Am/Eu} = 39.1 \pm 1.5$ at 0.1 M HNO$_3$. A decrease in both Am(III) and Eu(III) extraction was observed for (**8**) upon increasing HNO$_3$ concentration to both 1 M and 4 M (Fig. 5). D_{wAm} remained much greater than D$_{wEu}$ in both cases and at 4 M HNO$_3$ the extraction of Eu(III) dropped to $D_{wEu} \approx 3.3 \pm 0.4$ mL/g giving a separation factor $SF_{Am/Eu} \approx 57$. Although these results follow the same trend exhibited by CyMe$_4$-BTPhen ligands when immobilized onto other solid supported materials they are significantly lower than the results obtained for our previously studied model of CyMe$_4$-BTPhen SiO$_2$-coated MNPs at 4 M HNO$_3$ where a $SF_{Am/Eu} \approx 1700 \pm 300$ was obtained.[29] This may be due to the hydrophobic nature of the fibers.

The results for Am(III)/Cm(III) selective extraction by (**8**) are shown in Table 2 and Fig. 6. At low nitric acid concentration (0.001 M) there is a very little selectivity between Am(III) and Cm(III) ($SF_{Am/Cm} \approx 1.1$). An increase in extraction for both Am(III) and Cm(III) is observed upon increasing the concentration of HNO$_3$ to 0.1 M and at 1 M HNO$_3$, there is a more significant extraction of Am(III) over Cm(III) giving a separation factor of $SF_{Am/Cm} \approx 1.7$. Finally, at 4 M HNO$_3$, conditions akin to those found in reprocessing of spent nuclear fuel solution, a separation factor $SF_{Am/Cm} \approx 2.9$ is observed.

3. Conclusions

We have reported the synthesis of electro-spun polystyrene-immobilized CyMe$_4$-BTPhen fibers that will selectively extract Am(III) from Eu(III) at 4 M HNO$_3$ ($SF_{Am/Eu} > 57$). The fibers also exhibit a small but significant selectivity for Am(III) over its actinide neighbor Cm(III), with a separation factor of $SF_{Am/Cm} \approx 3$. The Am/Cm results are similar to separation factors achieved with previous solid supported ligands. The synthesis of novel 5-(4-vinylphenyl)-CyMe$_4$-BTPhen was achieved by adapting the recently reported selenium-free synthetic approach towards the core BTPhen structure. Installation of the 5-(4-vinylphenyl) group enabled efficient co-polymerization with styrene. Although the separation factor ($SF_{Am/Eu}$) this electro-spun polymer is lower than other previously reported solid supported ligands (e.g. MNPs and SiO$_2$), this could be attributed to the hydrophobicity of the fibers.

4. Experimental

4.1. Extraction studies

The aqueous solutions for the extraction experiments were prepared by spiking nitric acid solutions (0.001–4 M) with stock solutions of ^{241}Am, ^{152}Eu and ^{244}Cm and then adding 1.000 µL of spiked aqueous solution to accurately weighed 19.8 mg of BTPhen-polystyrene (**8**) (V/m ratio: 30.3 mL/g). The mixture was sonicated for 10 min and shaken (Heidolph Reax) at 1800 rpm for 90 min. After centrifuging for 2 min, aliquots of the aqueous solutions (supernatant) were separated and taken for measurements.

Activity measurements of ^{241}Am, ^{152}Eu and ^{244}Cm were performed with a γ-ray spectrometer EG&G Ortec (USA) with a PGT (USA) HPGe detector or α-ray spectrometer Octete plus Ortec (USA) with ion-implanted-silicon ultra α-detector (Ortec, USA). The weight distribution ratios, D_w, were calculated (Equation (1)), where A_o is the activity of the uncontacted aqueous phase, A_s is the activity of the aqueous phase after contact, w is the weight of (**8**) and V is the volume in contact with the sample [30]. These values

Table 2
Extraction of Am(III) and Cm(III) by (**8**) as a function of nitric acid concentration (*values are from alpha measurement). Mass of sorbent: accurately approximately 19.8 mg, phase volume: 1.0 mL, V/m ratio: ~30.3 mL/g.

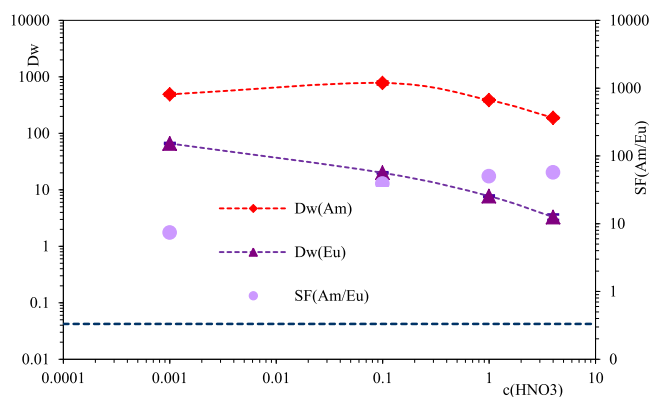| c(HNO$_3$)	D_w(Am)*	±		D_w(Cm)	±		SF(Am/Cm)	±	
0.001	371	±	43	343	±	27	1.1	±	0.2
0.1	543	±	68	441	±	39	1.2	±	0.2
1	350	±	39	204	±	12	1.7	±	0.2
4	151	±	14	53	±	3	2.9	±	0.6

Fig. 5. Extraction of Am(III) and Eu(III) by (**8**) as a function of nitric acid concentration. Mass of sorbent: accurately approximately 19.8 mg, phase volume: 1.0 mL, V/m ratio: ~30.3 mL/g.
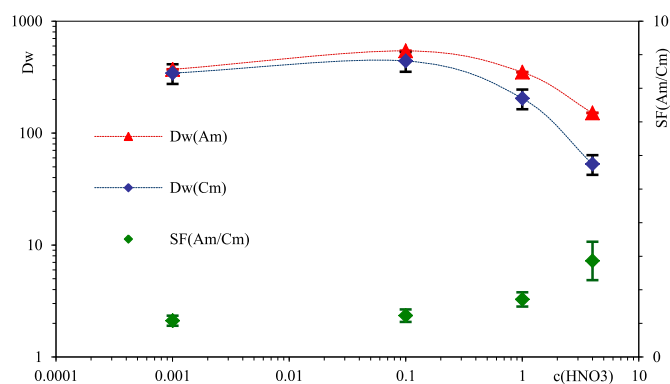

Fig. 6. Extraction of Am(III) and Cm(III) by (**8**) as a function of nitric acid concentration. Mass of sorbent: accurately approximately 19.8 mg, phase volume: 1.0 mL, V/m ratio: ~30.3 mL/g.

represent the ratio between the radioactivity (α- and γ-emissions) of each isotope in the standard solution and the supernatant. The separation factor is $SF_{Am/Eu} = D_{wAm}/D_{wEu}$ or $SF_{Am/Cm} = D_{wAm}/D_{wCm}$. Extractions were studied at nitric acid concentrations of 0.001 M, 0.1 M, 1 M and 4 M. All extraction experiments were carried out in duplicate and error bars in the figures represent standard deviations.

$$D_w = \frac{(A_o - A_s)}{A_s} \times \frac{v}{w} \tag{1}$$

4.2. General procedures

All reagents were purchased from AlfarAesar, Fisher or Sigma-Aldrich. All chemicals were of analytical grade and used as received without further purification unless otherwise stated. NMR

spectra were recorded using either a Bruker AMX400 or an Avance DFX400 instrument. Deuterated chloroform (CDCl$_3$) and Deuterated DMSO (dimethyl sulfoxide-d$_6$) were used as solvents. Chemical shifts (δ values) are reported in parts per million (ppm) with the abbreviations s, d, t, q, qn, sx, dd, dd and br denoting singlet, doublet, triplet, quartet, quintet, sextet, double doublet, double doublet and broad respectively. Coupling constants (J) are quoted in Hertz. FT-IR spectra were recorded on a Perkin Elmer RX1 FT-IR instrument. All the melting points were determined on a Gallenkamp melting point apparatus. Mass spectra were recorded under conditions of electrospray ionization (ESI). The ions observed were quasimolecular ions [MH]$^+$. The instrument used was a Thermo-Fisher Scientific LTQ orbitrap XL hybrid ion trap-orbitrap mass spectrometer.

4.3. Synthesis of 5-(4-vinylphenyl)-CyMe4-BTPhen (6)[26]

A suspension of Br-CyMe$_4$-BTPhen (**4**) (1.00 g, 1.60 mmol), tetrakis(triphenylphosphine)palladium(0) (74 mg, 0.05 mmol, 0.03 eq), 4-vinylphenylboronic acid (0.28 g, 1.90 mmol, 1.2 eq) and potassium carbonate (0.66 g, 4.8 mmol, 3 eq) in toluene (200 mL), EtOH (40 mL) and H$_2$O (40 mL) was heated to reflux for 48 h. The solution was then cooled to room temperature, diluted with water (250 mL) and extracted with CHCl$_3$ (3 × 100 mL). The organic extracts were collected and dried over MgSO$_4$ and concentrated *in vacuo*. The solid residue was triturated with Et$_2$O (100 mL) and filtered to give the title compound (**6**) as a yellow solid (0.55 g, 50%). M. p: decomposed at 280 °C. ^{1}H NMR (400 MHz, CDCl3) δ ppm 8.88 (d, $J = 8.3$ Hz, 1H), 8.79 (d, $J = 8.7$ Hz, 1H), 8.51 (d, $J = 8.6$ Hz, 1H), 8.46 (d, $J = 8.5$ Hz, 1H), 7.88 (s, 1H), 7.63 (d, $J = 8.2$ Hz, 2H), 7.57 (d, $J = 8.2$ Hz, 2H), 6.86 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.90 (d, $J = 17.6$ Hz, 1H), 5.38 (d, $J = 11.2$ Hz, 1H), 1.91 (s, 8H), 1.58 (s, 12H), 1.54 (s, 12H); ^{13}C NMR (101 MHz, CDCl3) δ ppm 164.99, 163.12, 161.56, 153.94, 146.79, 146.04, 139.57, 138.09, 137.61, 137.19, 136.26, 135.78, 130.21, 129.50, 129.0, 127.32, 126.56, 123.73, 123.16, 114.83, 77.36, 77.04, 76.72, 37.54, 36.62, 33.76, 29.86, 29.37; (FTMS + p ESI) cald. C$_{42}$H$_{45}$N$_8$Na [M+Na]$^+$: 661.3762; observed: 661.3747; FT-IR (ATR) νmax/cm^{-1} 2960 m, 2929 m, 2863 m, 1627w, 1515 m, 1470 m, 1454 m, 1359w, 1265 m, 1245 m.

4.4. Synthesis of polystyrene-immobilized CyMe$_4$-BTPhen (8)

Styrene **7** (4.0 g, 38 mmol) and AIBN (0.05 g, 0.3 mmol) were added to a polymerization tube followed by **6** (0.2 g, 0.3 mmol) and degassed. The tube was submerged in a water bath and heated to 55 °C for 18 h. The tube was cooled and the polymer formed was dissolved in DCM (50 mL) and then slowly added to cold MeOH (100 mL). The solid polymer that precipitated was then collected by filtration and dried in a vacuum oven at 40 °C to give the title compound as a yellow solid (2.5 g). % C, 88.83; H, 8.10; N, 2.44; M$_n$ = 361.0 and 7.0 kg mol^{-1} (Ð) = 1.95 and 2.00.

4.5. Electro-spinning of (8) into fibers

Electrospinning was performed using a Glassman's high voltage

power supply capable of delivering 0−30 kV with respect to ground. Solutions of **8** (1 g in 3 mL THF) were loaded into a 5 mL disposable plastic syringe fitted with a 21 gauge needle (0.514 mm nominal internal diameter) of length 40 mm to which the high voltage supply was attached. The solution flow rate was controlled by a Razel scientific syringe pump with flow rate set at approximately 2 mL h^{-1}. The distance between the flat aluminium collection plate and needle tip was 15 cm and an applied voltage of 15 kV was used for electrospinning. The room temperature at the time of spinning was ~21 °C and the relative humidity was 47%.

4.6. GPC analysis

Gel permeation chromatography (GPC) was conducted using an Agilent Technologies 1260 Infinity system and the data were processed using Agilent GPC/SEC software, with polystyrene being used as the calibrant. Samples for GPC analysis were dissolved in analytical grade THF (2 mg mL^{-1}) with butylated hydroxytoluene (BHT) stabilizer, and run using the same solvent as the mobile phase; eluting through two Agilent PLgel 5 μm MIXED-D 300 × 7.5 mm columns in series.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2018.04.037.

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