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Separation of Am(III) from Cm(III) and Eu(III) by electro-spun polystyrene-immobilized CyMe4-BTPhen

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Afsar, A., Westwood, J., Distler, P., Harwood, L. M. ORCID: https://orcid.org/0000-0002-8442-7380, Mohan, S., John, J. and Davis, F. J. ORCID: https://orcid.org/0000-0003-0462-872X (2018) Separation of Am(III) from Cm(III) and Eu(III) by electro-spun polystyrene- immobilized CyMe4-BTPhen. Tetrahedron, 74 (38). pp. 5258-5262. ISSN 0040-4020 doi: 10.1016/j.tet.2018.04.037 Available at https://centaur.reading.ac.uk/80776/

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To link to this article DOI: http://dx.doi.org/10.1016/j.tet.2018.04.037

Publisher: Elsevier

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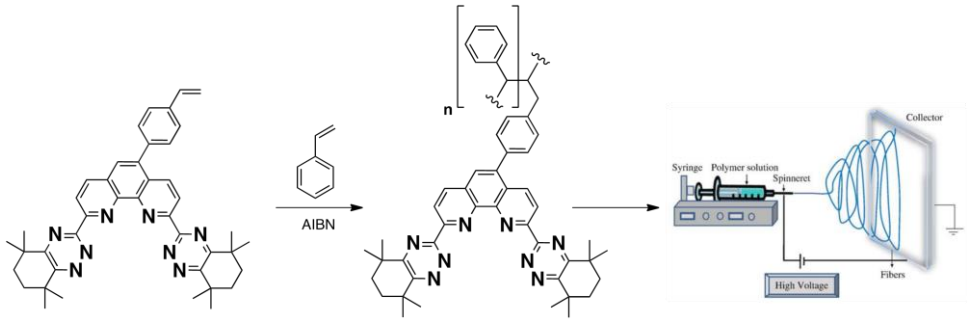

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Spent Nuclear Fuel
CyMe$_4$-BTPhen
Americium
Europium
Curium

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). The functionalized fibres demonstrated a separation factor of $SF_{Am/Eu}$ ~ 57 and a small, but significant separation of $SF_{Am/Cm}$ ~ 2.9 at 4 M HNO_3.

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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 radiotoxicity and heat-load of the fuel 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.[5,6]

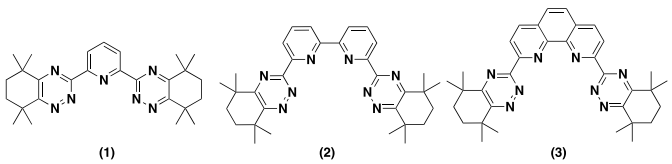


Fig 1. Structures of CyMe$_4$-BTP (**1**), CyMe$_4$-BTBP (**2**) and CyMe$_4$-BTPhen (**3**).

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.[7,8] 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 ligand efficiency for the extraction of the actinides over lanthanides by some electronically modulated ligands has been studied and reported.[9,10] Furthermore, 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.[11]

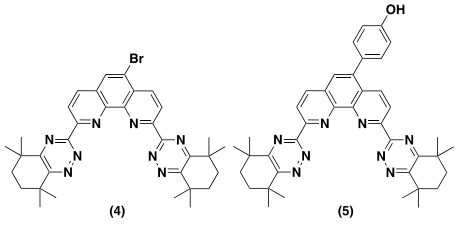
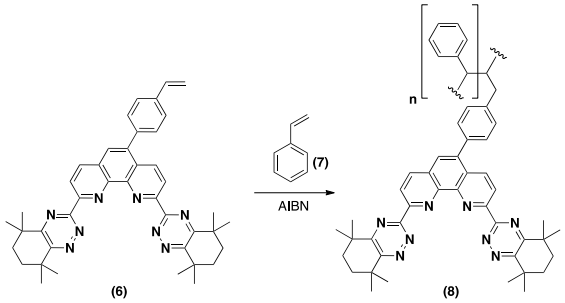


Fig. 2. Structures of Br-CyMe$_4$-BTPhen (**4**) and 5-(4-hydroxyphenyl)-CyMe$_4$-BTPhen (**5**)

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**) substitutents, revealing separation factors for Am(III) over Cm(III) ($SF_{Am/Cm}$) as high as 7.[9,10]

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 volumes of organic solvents and degradation of the solvents over time, resulting in reduced performance and efficiency. Quite often these liquid-liquid extraction systems require the use of phase modifiers to optimize extraction and third phase formation is usually encountered.[12] Extraction systems based on immobilized extractants would remove the need for an organic solvent. 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.[13,14] Related ligands have also been functionalized by cross-linking into PVB (polyvinyl benzyl) polymers and their Am(III) extraction ability investigated by use of an ion-exchange resin.[15] 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, will 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 electro-spun into fibres of polystyrene (**8**) (Scheme 1).

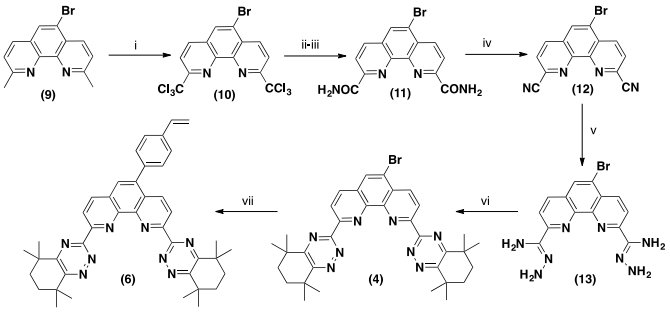


Scheme 1. Synthesis of Polystyrene immobilized $CyMe_4$-BTPhen (**8**)

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 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.[16] 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/methylation to give a *bis*-ester.[10,17] Conversion to a *bis*-amide and dehydration afforded the *bis*-nitrile compound required to develop BTPhen (**3**) related ligands.[14] 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.[18] Following these developments in the synthesis of BTPhen ligands, Br-$CyMe_4$-BTPhen (**4**) was synthesized using the improved synthetic protocol (Scheme 2).[10,14] 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.



Scheme 2. Synthesis of 5-(4-vinylphenyl)-$CyMe_4$-BTPhen (**6**): i) NCS, *m*-CPBA, $CHCl_3$, 90%; ii) H_2SO_4 then MeOH, 70%; iii) NH_4Cl, NH_4OH, 89%; iv) $POCl_3$, 90%; v) $N_2H_4.H_2O$ (64%), DMSO, 60%; vi) 3,3,6,6-tetramethylcyclohexan-1,2-dione, THF, Et_3N, 55%; vii) 4-vinylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, PhMe:EtOH:H_2O, 50%;

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).[19] 5-(4-Vinylphenyl)-$CyMe_4$-BTPhen (**6**) was subsequently co-polymerized with styrene using using AIBN as the initiator (Scheme 1). Electrospinning the 5-(4-vinylphenyl)-$CyMe_4$-BTPhen-styrene co-polymer (**8**) produced fine yellowish fibres, resembling cotton-wool.

2.2. Characterization of Electro-spun Fibers

The polystyrene-immobilized $CyMe_4$-BTPhen fibres (**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).

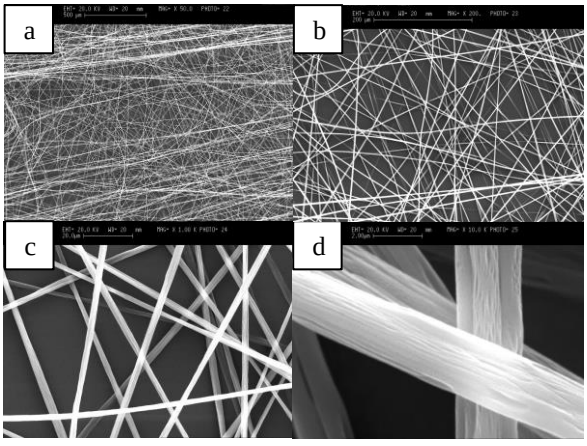


Fig 3. SEM images of polystyrene-immobilized $CyMe_4$-BTPhen fibres (**8**). Horizontal axis: a) 500 μm b) 200 μm c) 20 μm d) 2.0 μm

The SEM images at different magnifications clearly show the regularity in diameter and high surface area of these fine fibres 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 fibres (**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 Fig. 4. The overall distribution values revealed for M_n were 36.10 and 7.0 kg mol^{-1} respectively with dispersion values ($Đ$) of 1.95 and 2.00 respectively.

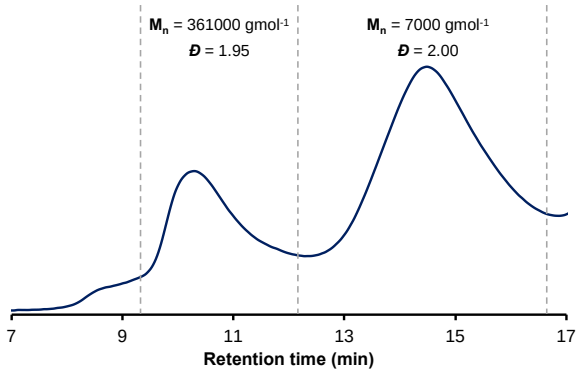


Fig. 4. GPC eluogram of polystyrene-immobilized CyMe$_4$-BTPhen fibres (**8**)

2.3. Extraction Data

The ability for polystyrene immobilized CyMe$_4$-BTPhen (**8**) to extract Am(III) from Eu(III) and Am(III) from Cm(III) across a range of HNO_3 concentration was investigated at the Czech Technical University in Prague. The extraction results for Am(III)/Eu(III) by (**8**) showed good distribution ratios for both Am(III) (D_{wAm} = 490 ± 24) and Eu(III) (D_{wEu} = 66 ± 1) at 0.001 M HNO_3 with a separation factor of $SF_{Am/Eu}$ = 7.40 ± 0.24 (Table 2). However, these values are much lower than those obtained for the same CyMe$_4$-BTPhen unit covalently bound to SiO_2-coated MNPs (D_{Am} = 1168.8 ± 79.1 and D_{Eu} = 701.4 ± 32.4).[20] Increasing the HNO_3 concentration led to an increase in Am(III) extraction (D_{wAm} = 781 ± 46), and a decrease in Eu(III) extraction (D_{wEu} = 20 ± 1) giving a separation factor of $SF_{Am/Eu}$ = 39.1 ± 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} ~ 3.3 ± 0.4 giving a separation factor $SF_{Am/Eu}$ ~ 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 $SF_{Am/Eu}$ ≈1700 ± 300 was obtained.[20] This may be due to the hydrophobic nature of the fibres.

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

Table 1. Extraction of Am(III) and Eu(III) by (**8**) as a function of nitric acid concentration

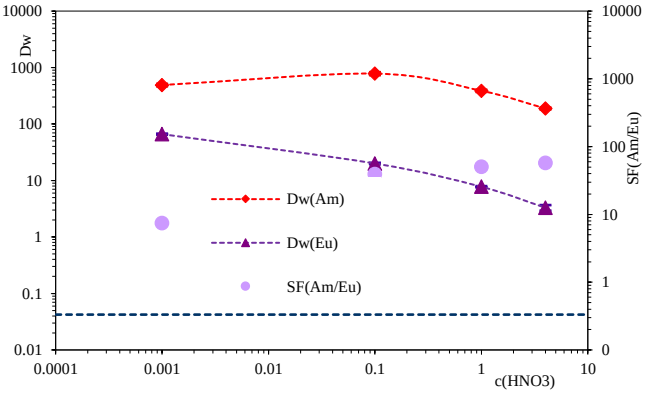


Fig. 5. Extraction of Am(III) and Eu(III) by (**8**) as a function of nitric acid concentration

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) ($SF_{Am/Cm}$ ~ 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 $SF_{Am/Cm}$ ~ 1.7. Finally, at 4 M HNO_3, conditions akin to those found in reprocessing of spent nuclear fuel, a separation factor $SF_{Am/Cm}$ ~ 2.9 is observed.

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

Table 2. Extraction of Am(III) and Cm(III) by (**8**) as a function of nitric acid concentration (*values are from alpha measurement)

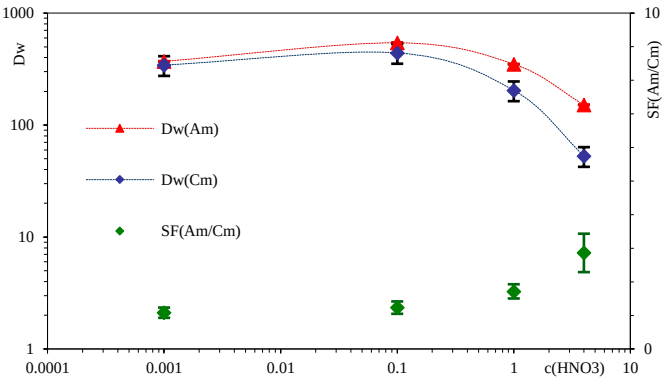


Fig. 6. Extraction of Am(III) and Cm(III) by (**8**) as a function of nitric acid concentration

3. Conclusions

We have reported the synthesis of electro-spun polystyrene-immobilized CyMe$_4$-BTPhen fibres that will selectively extract Am(III) from Eu(III) at 4 M HNO_3 ($SF_{Am/Eu}$ > 57). The fibres also exhibit exhibit a small but significant selectivity for Am(III) over its actinide neighbour Cm(III), with a of $SF_{Am/Cm}$ ~ 3. The Am/Cm results are similar to separation factors achieved with other 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 of 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 fibres.

4. Experimental

4.1. Extraction Studies

The aqueous solutions for the solvent 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 19.8 mg of BTPhen-polystyrene (**8**) (V/m ratio: 30.3 mL g^{-1}). 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.

Quantitative measurements of the distribution weight 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.[21] These values represent the ratio between the radioactivity (α- and γ- emissions) of each isotope in the standard solution and the supernatant. The separation factor is $SF_{Am/Eu} = D_{Am} / D_{Eu}$ or $SF_{Am/Cm} = D_{Am} / D_{Cm}$. Extractions were studied at nitric acid concentrations of 0.001 M, 0.1 M, 1 M and 4 M.

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

4.2. General Procedures

All reagents were purchased from Alfar, 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, ddd and br denoting singlet, doublet, triplet, quartet, quintet, sextet, double doublet, double double doublet and broad respectively. Coupling constants (*J*) are quoted in Hertz. 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 an Xcalibur Tune 2.1 (SP1).

*4.3. Synthesis of 5-(4-vinylphenyl)-CyMe$_4$-BTPhen (**6**)*[22]

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_2O (40 mL) was heated to reflux for 48 hr. The solution was then cooled to room temperature, diluted with water (250 mL) and extracted with $CHCl_3$ (3 x 100 mL). The organic extracts were collected and dried over $MgSO_4$ and concentrated *in vacuo*. The solid residue was triturated with Et_2O (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 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 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; **MASS SPECTRUM/ ? INFRA RED**

*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 degassed MeOH (100 mL). **6** (0.2 g, 0.3 mmol) was added and the tube was submerged in a water bath and heated to 55 °C for 18 hr. 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).

*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 hr^{-1}. The distance between the flat aluminium collection plate and needle tip was 15 cm and the 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

Use of the Chemical Analysis Facility (CAF) and the Electron Microscopy Laboratory (EMLab) at the University of Reading is gratefully acknowledged. We thank Mr Tahkur Singh Babra for running GPC analysis on the fibres.

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