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Synthesis of Polyarylamines via Microwave Assisted Palladium-catalysed Amination

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Polytriarylamines comprising 5 to 20 repeat units are thought to have suitable charge transport characteristics for electrooptical applications.[s1] Therefore, the ratio of 2,4-dimethylaniline to 4,4'-dibromobiphenyl was varied in several experiments to determine the optimal monomer ratio to produce a polymer of optimal molecular weight. Table 1 shows both the GPC determined number-averaged molecular weight (M_n) and the weight-averaged molecular weight (M_w) of the polymer obtained from polymerising various ratios of 2,4-dimethylaniline and 4,4'-dibromobiphenyl.

The polymerisation of an increasing ratio of 2,4-dimethylaniline relative to 4,4'-dibromobiphenyl gave a concomitant reduction in both M_n and M_w of the resultant polymer. The polymerisation reaction that employed a 1:1 ratio of amine to bromide provided a polymer in 70 % yield that had the largest M_n (2169) and M_w (6357) of the three polymers **S1**-**S3** synthesised, which corresponds to polymer **1** comprising 8 repeat units (Table S-1, polymer **S1**).

Table S-1. GPC data of polytriarylamines **S1**-**S3**.

Polymer	Amine:bromide	M_n	$M_n/271$ [a)]	M_w	M_w/M_n
S1	1:1	2169	8.00	6357	2.93
S2	1.1:1	1777	6.56	4863	2.74
S3	1.5:1	930	3.43	1590	1.71

[a)] Corresponds to the number of monomer repeat units.

The polymerisation reaction mixture for preparation of **S1** was analysed by GC-MS, and this identified the incomplete reaction of 4,4'-dibromobiphenyl. In addition, the GPC trace of polymer **S1** revealed a polydispersity value of 2.93, suggesting that there may be a significant amount of low molecular weight material present. Therefore, 2,4-dimethylaniline was purified by distillation to improve the stoichiometry of the monomers.

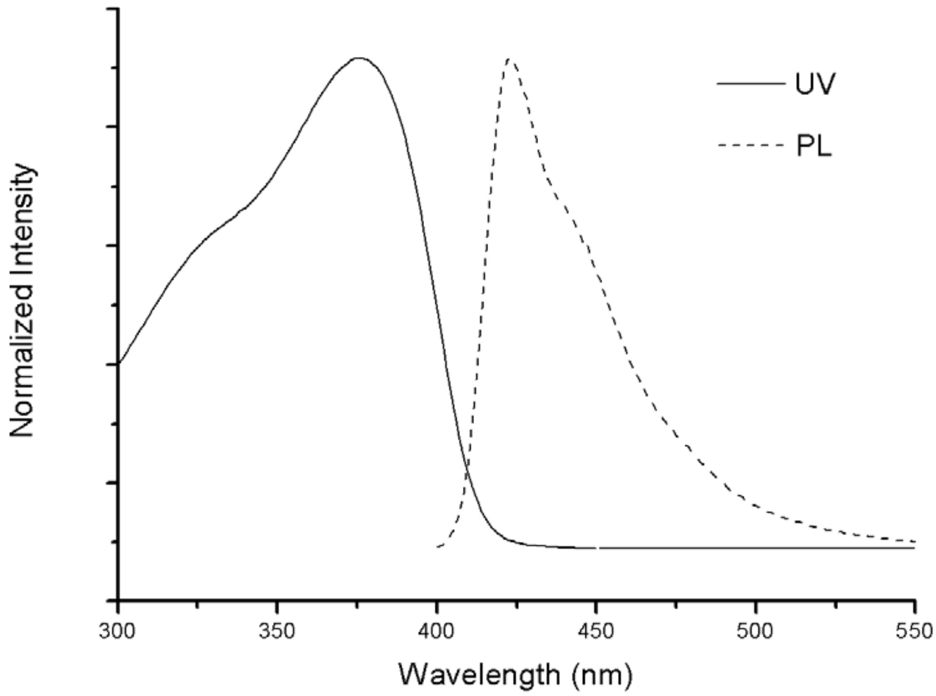

Figure S-1. UV-Vis and photoluminescence spectra of polymer **2**. UV (dichloromethane): λ_{max} = 378 nm (261 991 $L\cdot mol^{-1}\cdot cm^{-1}$). PL (dichloromethane): λ_{max} = 423 nm (excitation wavelength = 378 nm).

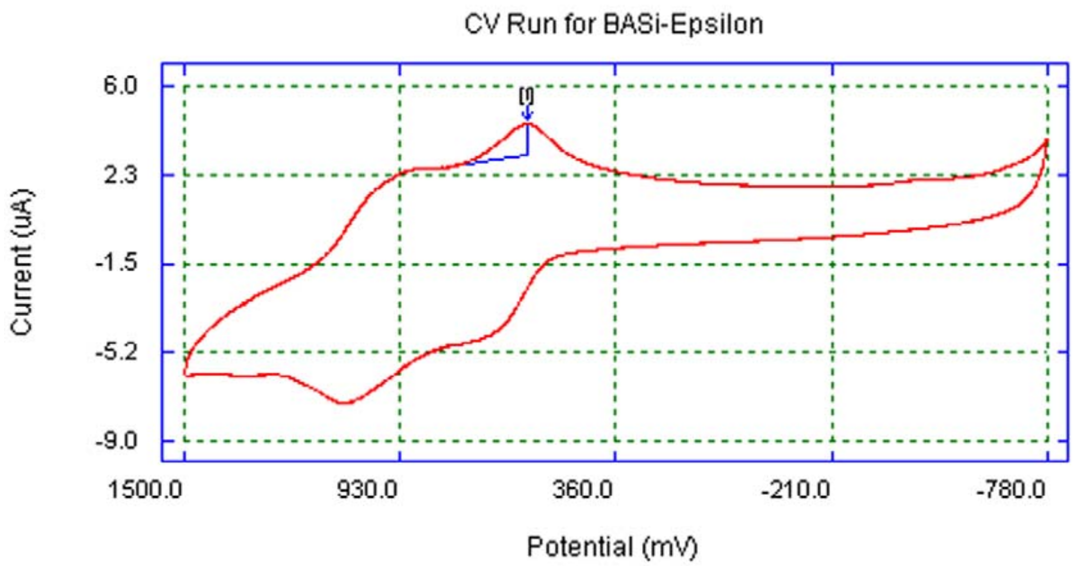

Figure S-2. Cyclic voltammetry spectrum of polymer **2**.

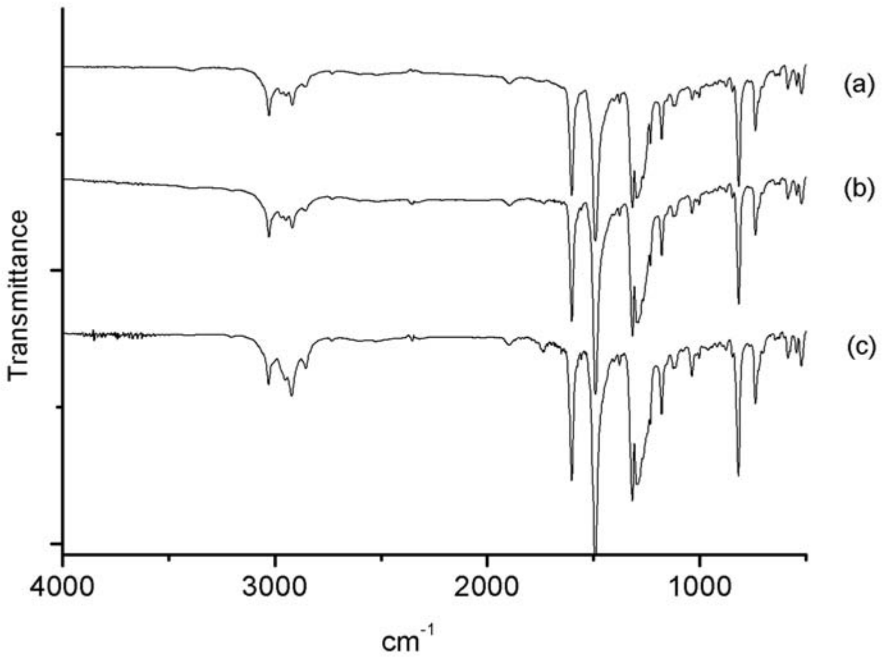

Figure S-3. IR spectra of (a) Uncapped polymer **2**. (b) Polymer **15** following the first end-capping with 4-bromoanisole. (c) Polymer **15** following the second end-capping with 4-bromoanisole.

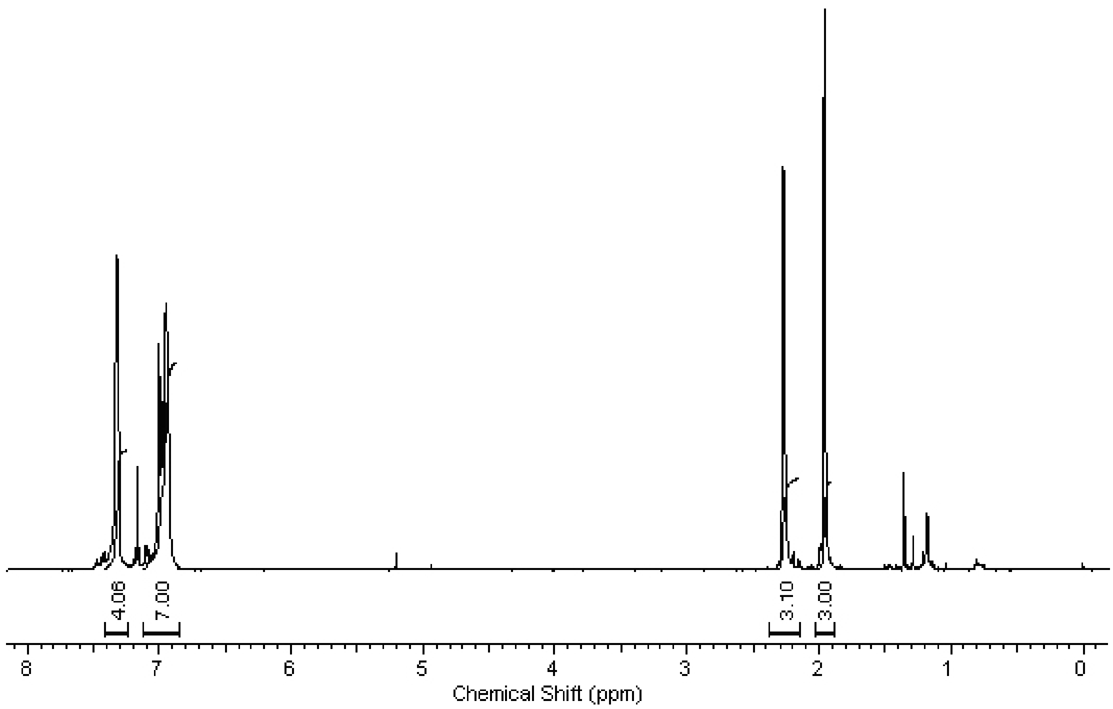

Figure S-4. [1]H NMR spectrum of uncapped polymer **2**.

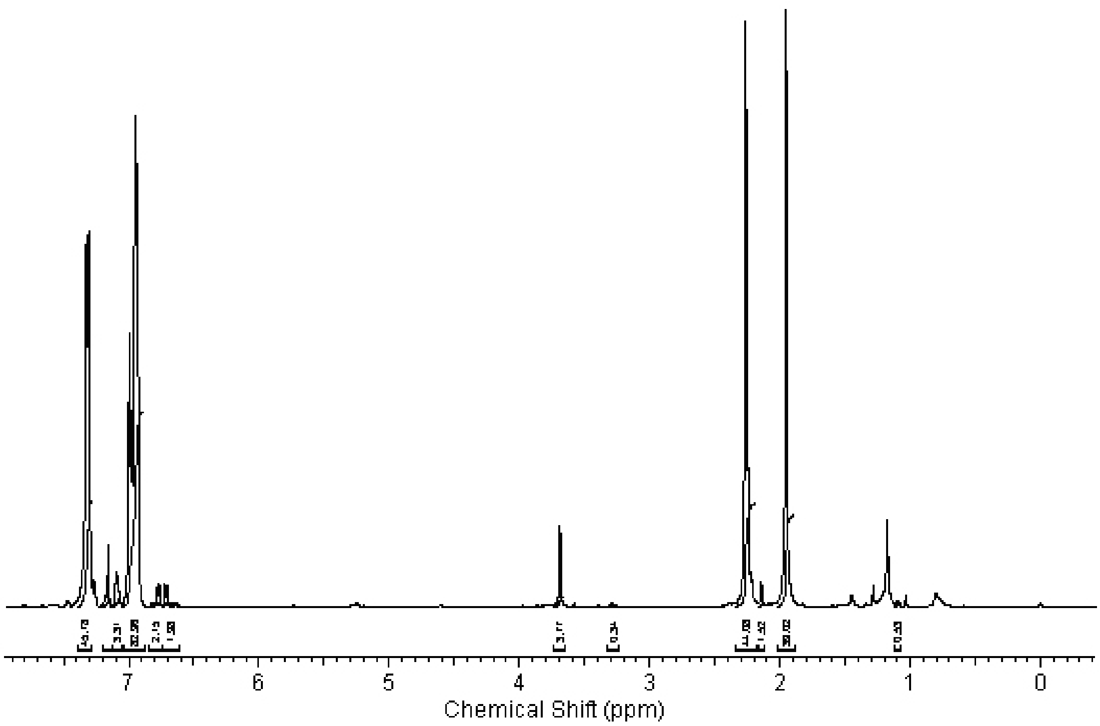

Figure S-5. [1]H NMR spectrum of end-capped polymer **15**.

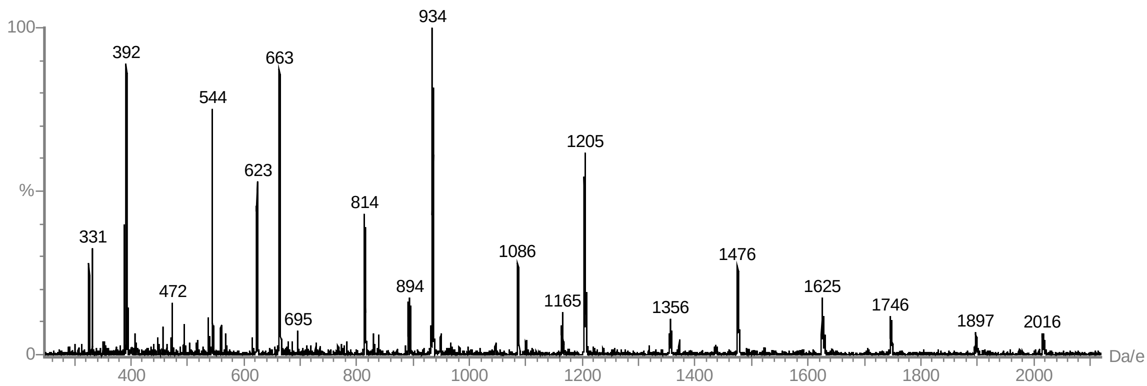

Figure S-6. MALDI-TOF spectrum of uncapped polymer **2**.

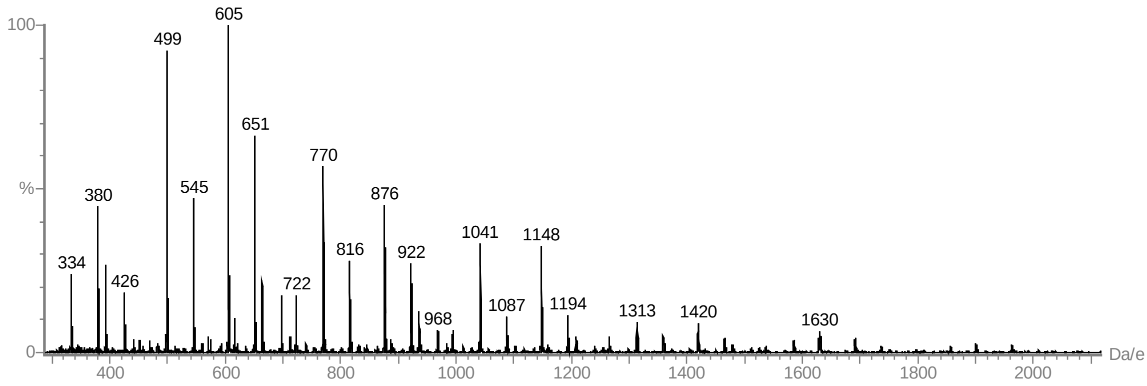

Figure S-7. MALDI-TOF spectrum of end-capped polymer **15**.