Supplementary material (ESI) for Journal of Materials Chemistry

Supplementary Information

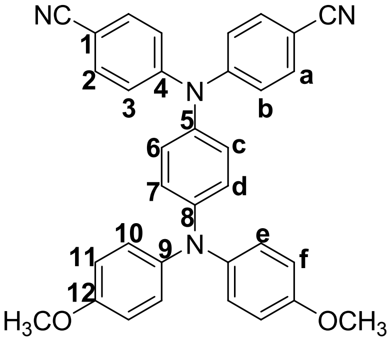
Novel anodic electrochromic aromatic polyamides with multi-stage oxidative coloring based on *N,N,N',N'*-tetraphenyl-*p*-phenylenediamine derivatives

Cha-Wen Chang[a] **and Guey-Sheng Liou***[b]

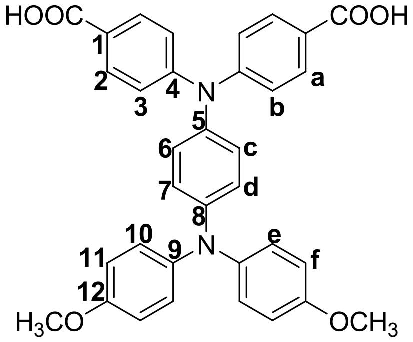
[a] *Department of Applied Chemistry, National Chi Nan University, 1 University Road, Puli, Nantou Hsien 54561, Taiwan, Republic of China.*
[b] *Institute of Polymer Science and Engineering, National Taiwan University, Taipei, 10617, Taiwan, Republic of China.*

Monomer synthesis

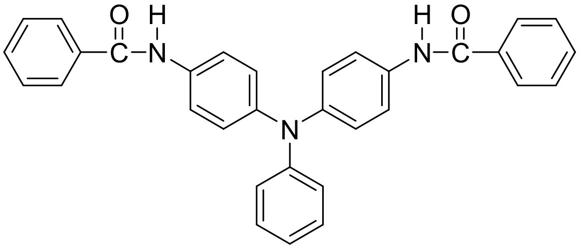
***N,N*-Bis(4-cyanophenyl)-*N',N'*-di(4-methoxyphenyl)-1,4-phenylenediamine (3).** A mixture of 0.55 g (23 mmol) of sodium hydride and 40 mL of DMF was stirred, under nitrogen, at room temperature for about 30 min, and then 3.20g (10 mmol) of compound (**2**) were added. After the evolution of hydrogen was complete, 2.54 g (21 mmol) of 4-fluorobenzonitrile were added and the temperature maintained for 15 h at 150 ℃. Next, the reaction mixture was poured into water, the crude product collected by filtration, and purified by washed with hexane/ethyl acetate to give 1.57 g (30 % in yield) of yellowish powder. Mp = 192-194 ℃ measured by DSC at 10 °C/min. IR (KBr): 2951, 2834 cm^{-1} (OCH_3 C-H stretch), 2223 cm^{-1} (C≡N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 3.72 (s, 6H, OCH_3), 6.76 (d, 2H, H_d), 6.91 (d, 4H, H_f), 6.97 (d, 2H, H_c), 7.07 (d, 4H, H_e), 7.09 (d, 4H, H_b), 7.68 (d, 4H, H_a). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 55.4 (OCH_3), 104.1 (C^1), 115.2 (C^{11}), 119.2(CN), 119.9 (C^7), 122.1 (C^3), 127.3 (C^{10}), 128.6 (C^6), 133.9 (C^2), 136.0 (C^8), 139.8 (C^9), 147.4 (C^5), 150.1 (C^4), 156.3 (C^{12}).



_N,N_-Bis(4-carboxyphenyl)-_N',N'_-di(4-methoxyphenyl)-1,4-phenylenediamine (4). A mixture of 6.00 g (107 mmol) of potassium hydroxide and 2.61 g (5 mmol) of the dinitrile compound (**3**) in 50 mL of ethanol and 25 mL of distilled water was stirred at about 100 ℃ until no further ammonia was generated. The time taken to reach this stage was about 5-6 days. The solution was cooled, and the pH value was adjusted by hydrochloric acid to near 3. The yellowish precipitate formed was collected by filtration and purified by recrystallization from acetic acid to give 2.25 g (80 % in yield) of the pure diacid. Mp: 323-324 ℃ measured by DSC at 10 °C/min. IR (KBr): 2700-3400 cm^{-1} (O-H), 1682 (C=O). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 3.71 (s, 6H, OCH_3), 6.76 (d, 2H, H_d), 6.89 (d, 4H, H_f), 6.95 (d, 2H, H_c), 7.04 (d, 4H, H_b), 7.06 (d, 4H, H_e), 7.82 (d, 4H, H_a), 12.61 (br, 2H, COOH). ^{13}C NMR (100 Hz, DMSO-d_6, δ, ppm): 55.4 (OCH_3), 115.2 (C^{11}), 120.2 (C^7), 121.5 (C^3), 124.2 (C^1), 127.2 (C^{10}), 128.2 (C^6), 131.1 (C^2), 137.1 (C^8), 140.0 (C^9), 146.7 (C^5), 150.6 (C^4), 156.1 (C^{12}), 167.0 (C=O). Anal. Calcd for $C_{34}H_{28}N_2O_6$ (560.59): C, 72.84 %; H, 5.03 %; N, 5.00 %. Found: C, 72.74 %; H, 5.03 %; N, 5.00 %.

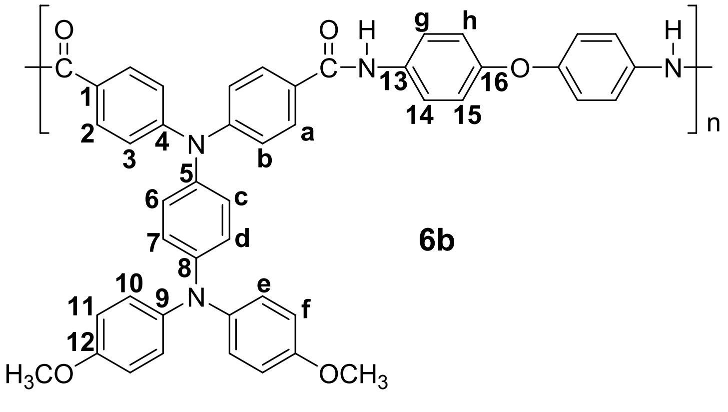


4,4’-diamidetriphenylamine (M2). A mixture of 0.275 g (1.00 mmol) of 4,4’-diaminoltriphenylamine, 0.256g (2.10 mmol) of benzoic acid, , 1.00 mL of triphenyl phosphite (TPP), 0.5 mL of pyridine (Py) and 1.00 mL of NMP was heated with stirring at 105 °C for 3 h. The mixture was poured slowly into 50 mL of stirring methanol washed, then was collected by filtration, and dried under vacuum at 100 °C; yield: 0.459 g (95 %). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 6.95–7.03 (m, 7H, Ar), 7.26 (t, 2H, Ar), 7.49–7.58 (m, 6H, Ar), 7.74 (d, 4H, Ar), 7.93 (d, 4H, Ar). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 121.9, 122.1, 122.4, 124.5, 127.8, 128.5, 129.5, 131.6, 134.7, 135.2, 143.2, 147.8, 165.5.



Polymer synthesis

The synthesis of polyamide **6b** is used as an example to illustrate the general synthetic route. The typical procedure was as follows. A mixture of 0.500 g (0.89 mmol) of the dicarboxylic acid monomer (**4**), 0.179 g (0.89 mmol) of 4,4’-oxydianiline, 0.10 g of calcium chloride, 0.90 mL of TPP, 0.45 mL of Py, and 1.0 mL of NMP was heated with stirring at 105 ℃ for 3 h. The polymer solution was poured slowly into 300 mL of stirring methanol giving rise to a stringy, fiber-like precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried under vacuum at 100 °C; yield: 0.640 g (99 %). Precipitations from DMAc into methanol were carried out twice for further purification. The inherent viscosity of the obtained polyamide **6b** was 0.83 dL/g, measured at a concentration of 0.5 g/dL in NMP at 30 ℃. The IR spectrum of **6b** (film) exhibited characteristic amide absorption bands at 3414 cm^{-1} (N-H stretch), 3038 cm^{-1} (aromatic C-H stretch), 2932, 2834 cm^{-1} (OCH_3 C-H stretch), 1654 cm^{-1} (amide carbonyl), 1240 cm^{-1} (asymmetric stretch C-O-C), 1033 cm^{-1} (symmetric stretch C-O-C). ^1H NMR (300 MHz, DMSO-d_6, δ, ppm): 3.72 (s, 6H, OCH_3), 6.80 (d, 2H, H_d), 6.91 (d, 4H, H_f), 6.99 (d, 4H, H_h), 6.99 (d, 2H, H_c), 7.06 (d, 4H, H_e), 7.09 (d, 4H, H_b), 7.74 (d, 4H, H_g), 7.88 (d, 4H, H_a), 10.13 (s, 2H, NH-CO). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 55.45 (OCH_3), 115.2 (C^{11}), 118.8 (C^{15}), 120.5 (C^7), 121.6 (C^3), 122.2 (C^{14}), 127.0 (C^{10}), 128.0 (C^6), 128.4 (C^1), 129.4 (C^2), 135.1 (C^{13}), 137.9 (C^8), 140.2 (C^9), 146.4 (C^5), 149.8 (C^4), 152.9 (C^{16}), 156.1 (C^{12}), 164.9 (NH-CO). Anal. Calcd for $(C_{46}H_{36}N_4O_5)_n$ $(724.80)_n$: C, 76.23 %; H, 5.01 %; N, 7.73 %. Found: C, 74.99 %; H, 5.15 %; N, 7.70 %. The other polyamides were prepared by an analogous procedure.



6b

Results and discussion

Monomer synthesis

The new aromatic dicarboxylic acid *N,N*-bis(4-carboxyphenyl)-*N',N'*-di(4-methoxyphenyl)-1,4-phenylenediamine (**4**), having bulky pendent 4,4'-dimethoxytriphenylamine group, was synthesized in four steps starting from the aromatic nucleophilic substitution reaction of 4-nitroaniline with 4-iodoanisole produced 4-nitro-4',4"-dimethoxytriphenylamine (**1**) (Scheme 1). 4-amino-4',4"-dimethoxytriphenylamine (**2**) was prepared by hydrazine Pd/C-catalyzed reduction of the intermediate compound, 4-nitro-4',4"-dimethoxytriphenylamine (**1**). The double-coupling reaction of the conjugate base of **2** (1.0 equiv) with 4-fluorobenzonitrile (2.1 equiv) produced *N,N*-bis(4-cyanophenyl)-*N',N'*-di(4-methoxyphenyl)-1,4-phenylenediamine (**3**). The alkaline hydrolysis of the dinitrile compound **3** afforded the target dicarboxylic acid monomer **4**. Elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopic techniques were used to identify the structures of the dicarboxylic acid monomer **4**. The IR spectra of dinitrile compound **3** gave a characteristic sharp band at 2223 cm^{-1} peculiar to the cyano group. After hydrolysis, the characteristic absorption of the cyano group disappeared, and the carboxylic acid group showed a typical carbonyl absorption band at 1682 cm^{-1} (C=O stretching) together with the appearance of broad bands around 2700-3400 cm^{-1} (O-H stretching). Fig. S1 and S2 illustrate the ^{1}H NMR and ^{13}C NMR spectra of compounds **3** and **4**, respectively. Assignments of each carbon and proton of monomer **4** are assisted by the two-dimensional (2D) NMR spectra (Fig. S3 and S4**)**, and these spectra agree well with the proposed molecular structures of **4**. The ^{13}C NMR spectra confirm that the cyano groups were completely converted into the carboxylic acid groups by the disappearance of the resonance peak for the cyano carbon at 119.2 ppm and by the appearance of the carbonyl peak at 167.0 ppm. Other important evidence of this change is the shifting of the carbon resonance signals of C^1 adjacent to the cyano or carboxyl group. The C^1 carbons of dinitrile **3** resonated at a higher field (104.1 ppm) than the other aromatic carbons because of the anisotropic shielding by the π electrons of $C{\equiv}N$. After hydrolysis, the resonance peak of C^1 shifted to a lower field (124.2 ppm) because of the lack of an anisotropic field.

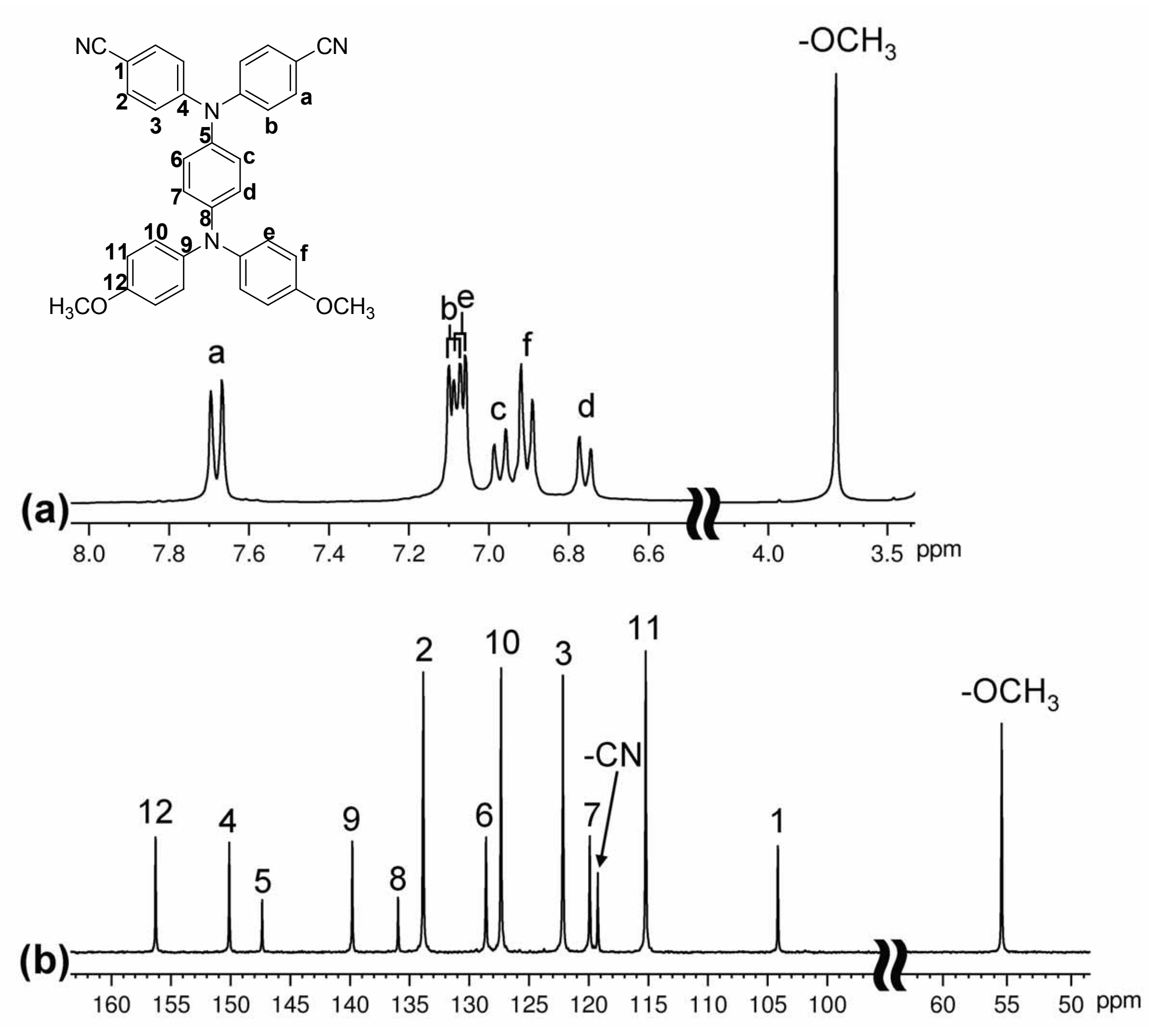


Fig. S1 (a) ^{1}H NMR and (b) ^{13}C NMR spectrum of compound **3** in DMSO-d_6.

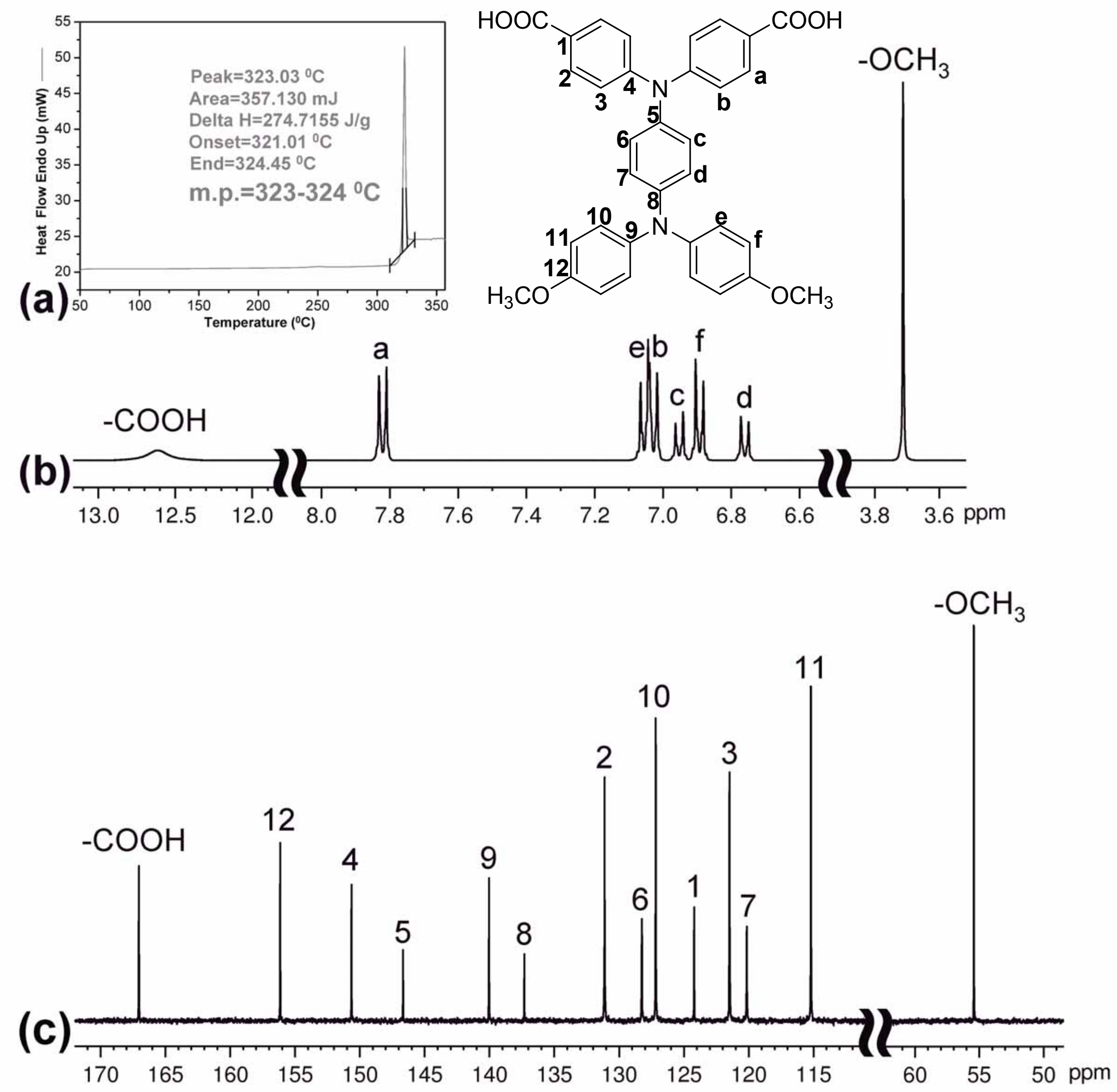


Fig. S2 (a) A typical DSC curve with a heating rate of 10 °C/min, (b) ^{1}H NMR, and (c) ^{13}C NMR spectrum of compound **4** in DMSO-*d*$_6$.

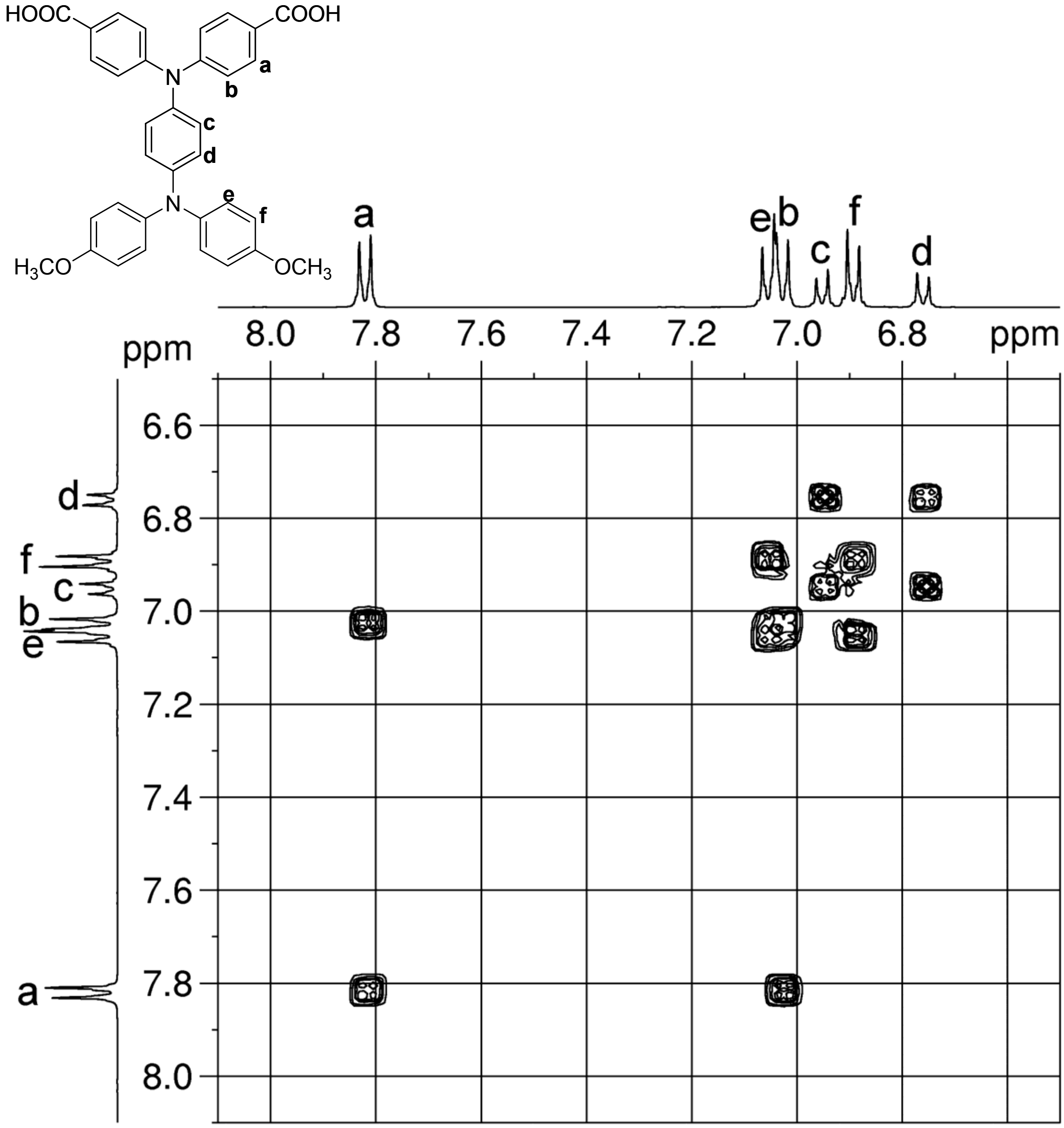


Fig. S3 H-H COSY spectrum of compound **4** in DMSO-d_6.

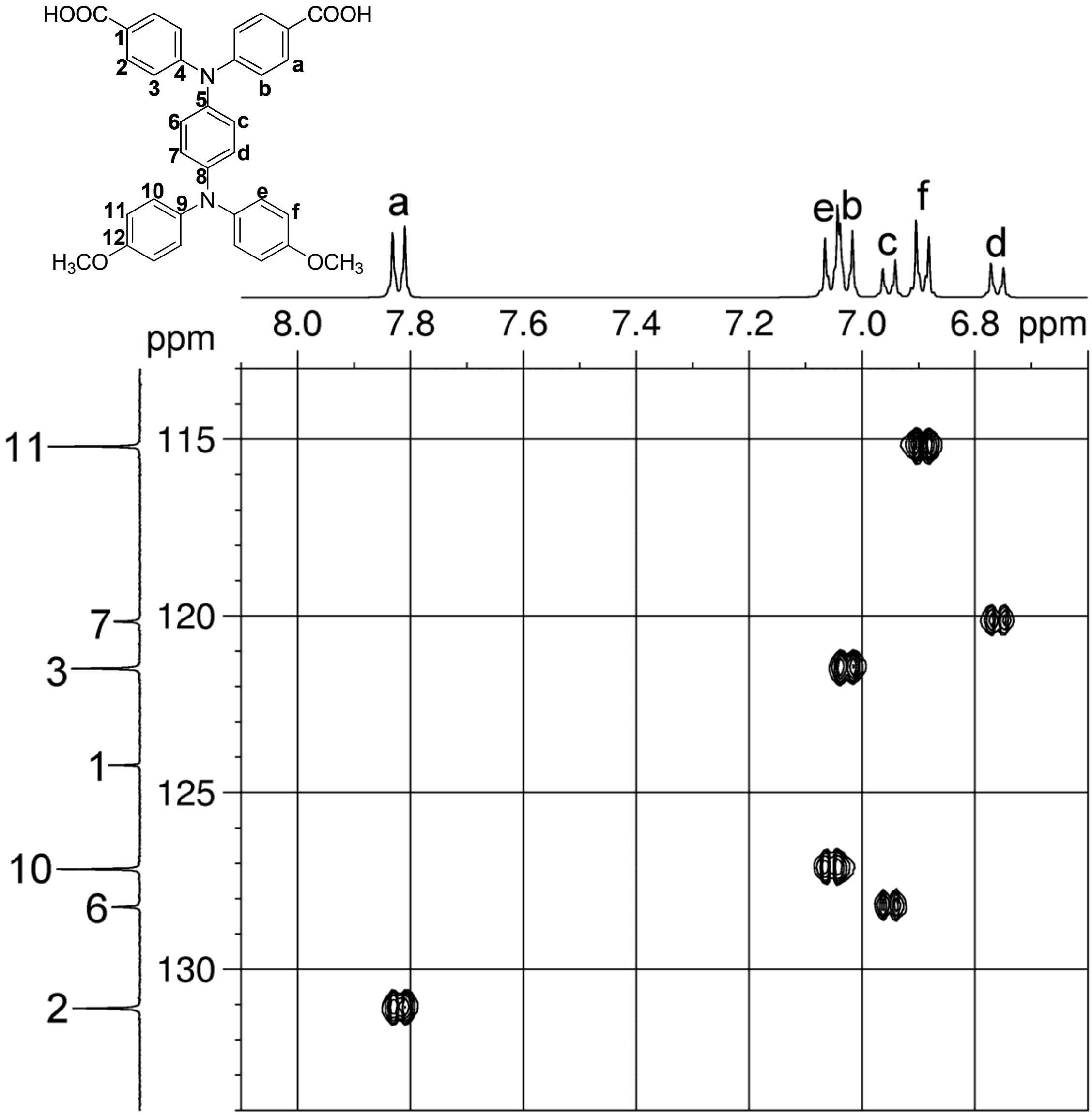


Fig. S4 C-H HMQC spectrum of compound **4** in DMSO-d_6.

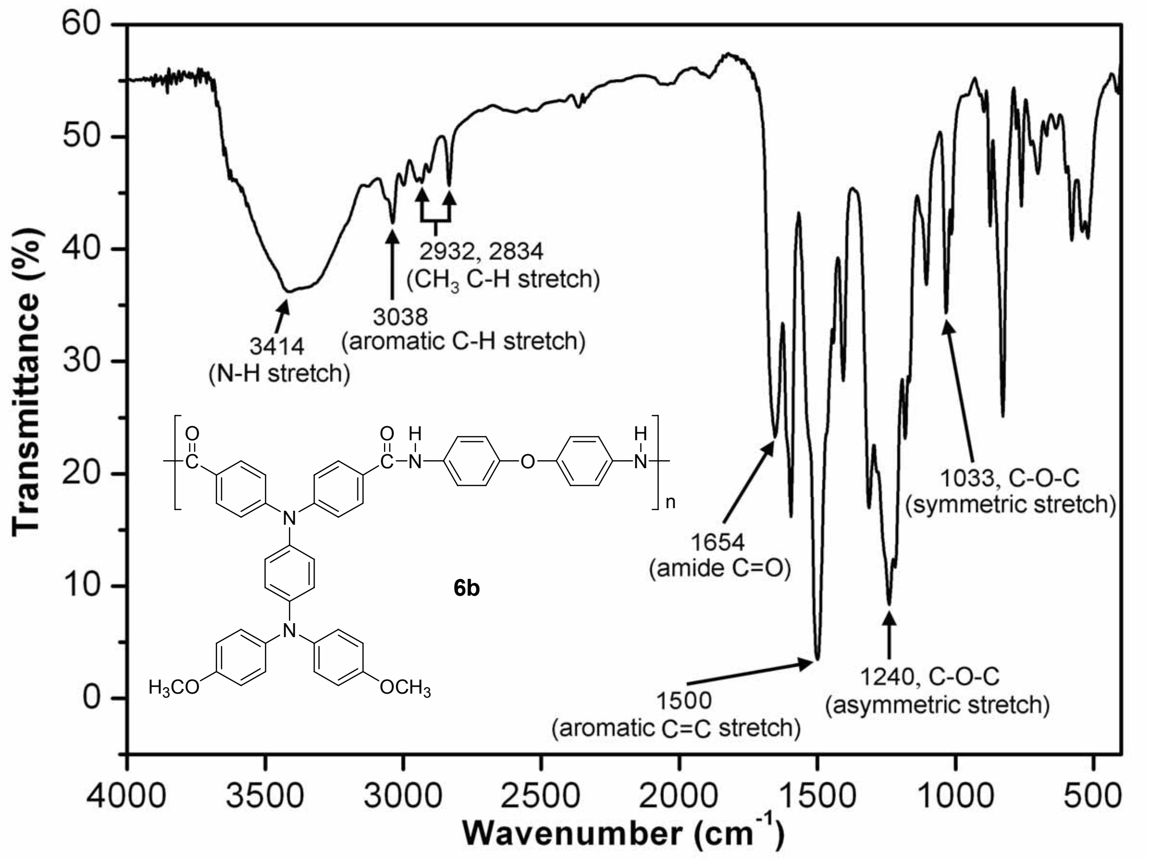


Fig. S5 IR spectrum of polyamide **6b** film.

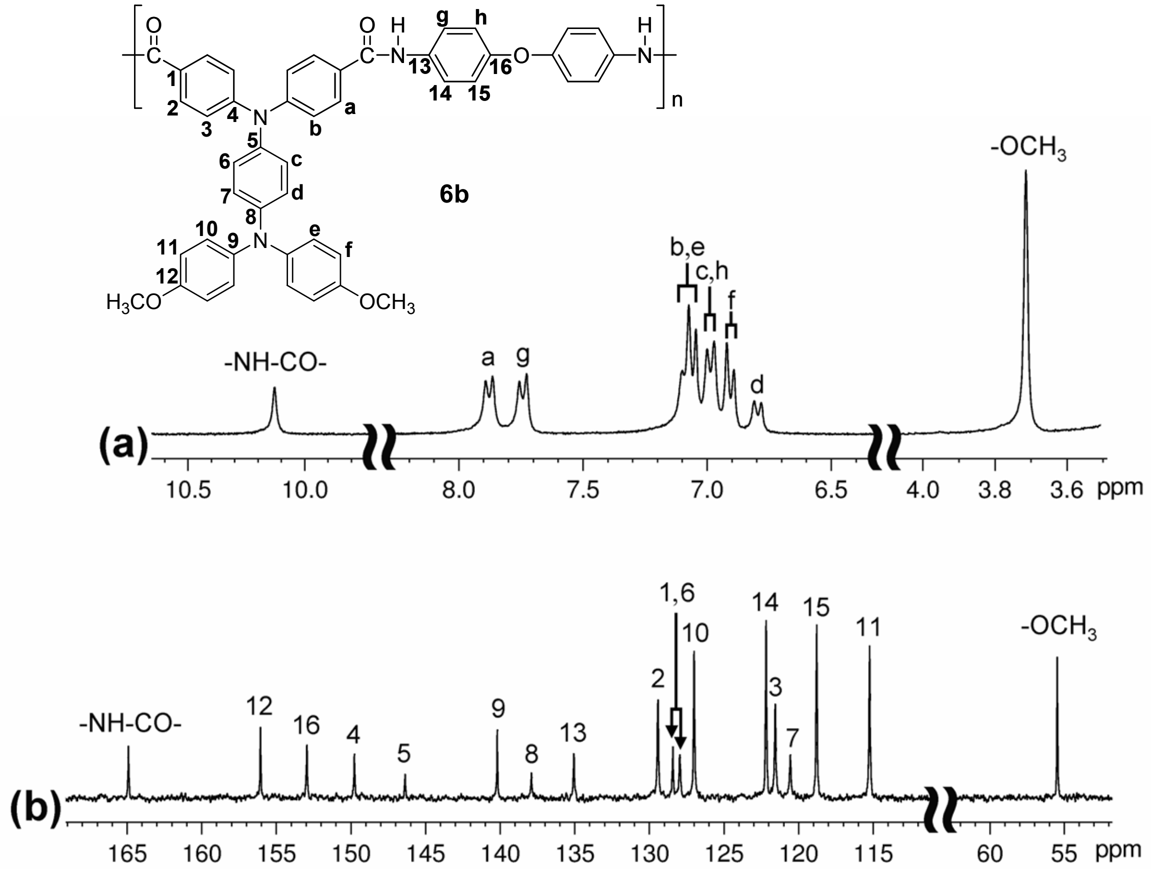


Fig. S6 (a) ^{1}H NMR and (b) ^{13}C NMR spectrum of polyamide **6b** in DMSO-d_6.

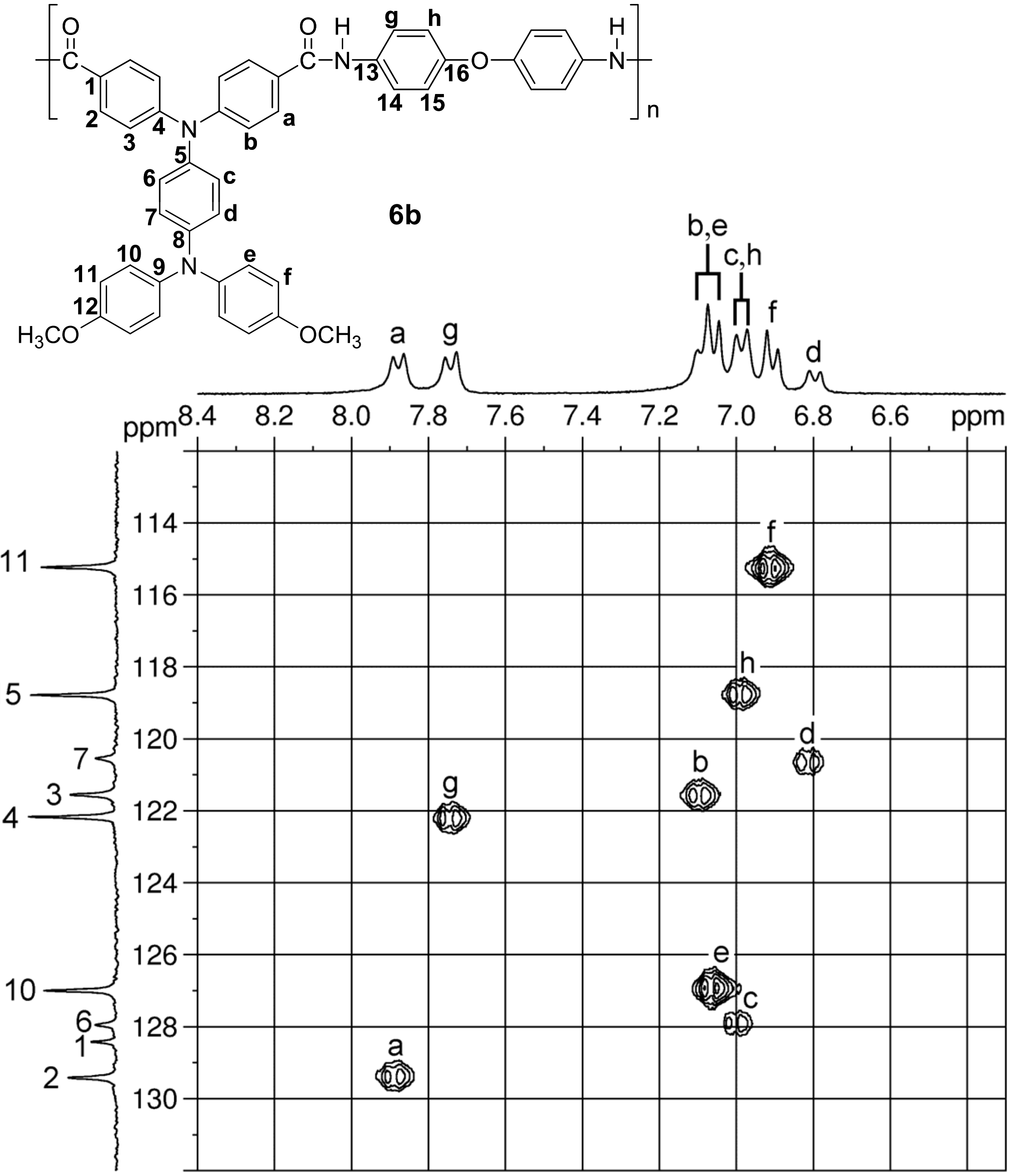


Fig. S7 C-H HMQC spectrum of polyamide **6b** in DMSO-d_6.

Polymer	Solvents						
	NMP	DMAc	DMF	DMSO	*m*-cresol	THF	$CHCl_3$
6a	+ +	+ +	+	+ +	+ +	±	±
6b	+ +	+ +	+	+ +	+ +	—	—
6c	+ +	+ +	+ +	+ +	+ +	±	±
6d	+ +	+ +	+ +	+ +	+ +	+ +	±
6e	+ +	+ +	+ +	+ +	+ +	±	±
6f	+ +	+ +	+ +	+ +	+ +	+ +	±
6g	+ +	+ +	+ +	+ +	+ +	±	±

Table S1 Solubility[a] of polyamides

[a] Qualitative solubility was tested with 1 mg of a sample in 1 mL of stirred solvent. + +, soluble at room temperature; +, soluble on heating; ±, partially soluble; —, insoluble even on heating.

Polymer	η_{inh}[a] (dL/g)	*Mw*[b]	*Mn*[b]	PDI
6a	0.40	41,000	23,000	1.80
6b	0.83	66,000	33,000	1.98
6c	0.42	67,000	35,000	1.92
6d	0.29	36,000	19,000	1.87
6e	0.30	44,000	23,000	1.95
6f	0.24	34,000	18,000	1.93
6g	0.31	40,000	21,000	1.91

Table S2 Inherent viscosities and GPC data of polyamides

[a] Measured at a polymer concentration of 0.5 g/dL in NMP at 30 °C.

[b] Relative to polystyrene standards, using DMF as the eluent.

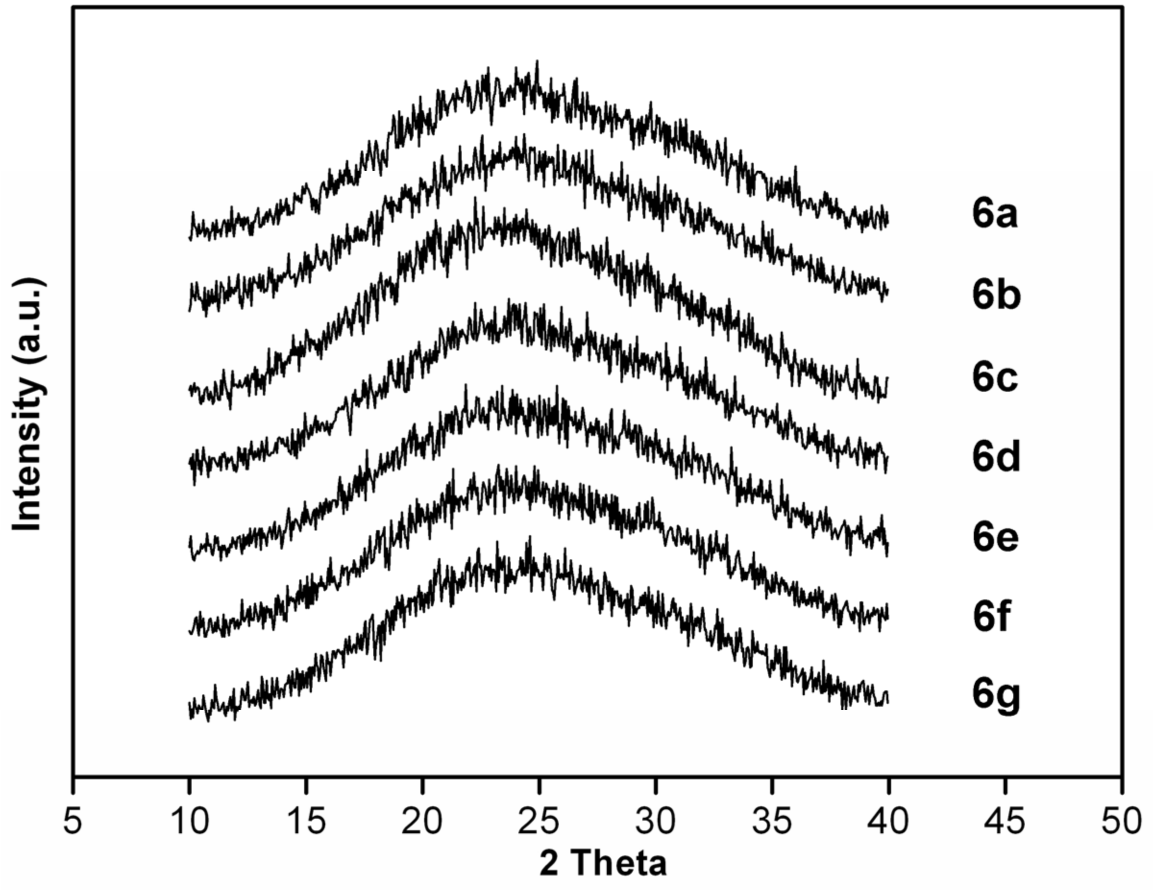


Fig. S8 WAXD patterns of the polyamide films.

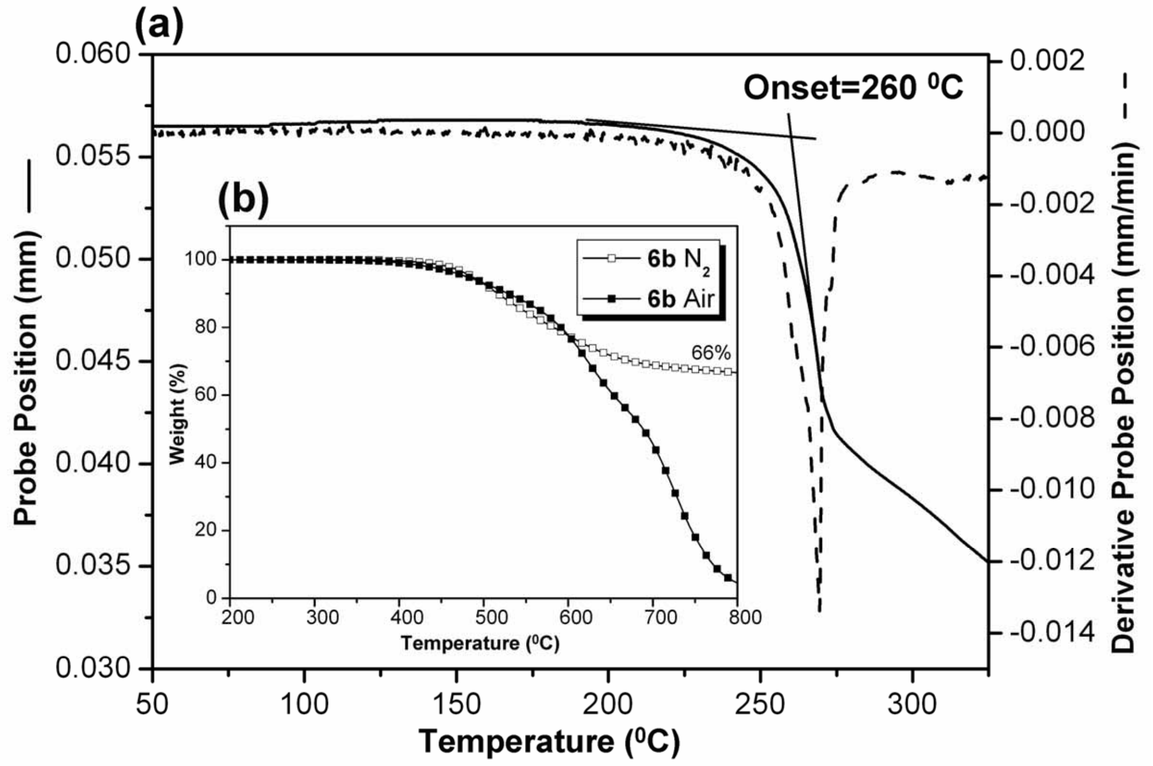


Fig. S9 (a) TMA curve of polyamide **6a** with a heating rate of 10 °C/min and (b) TGA thermograms of polyamide **6b** at a scan rate of 20 °C/min.

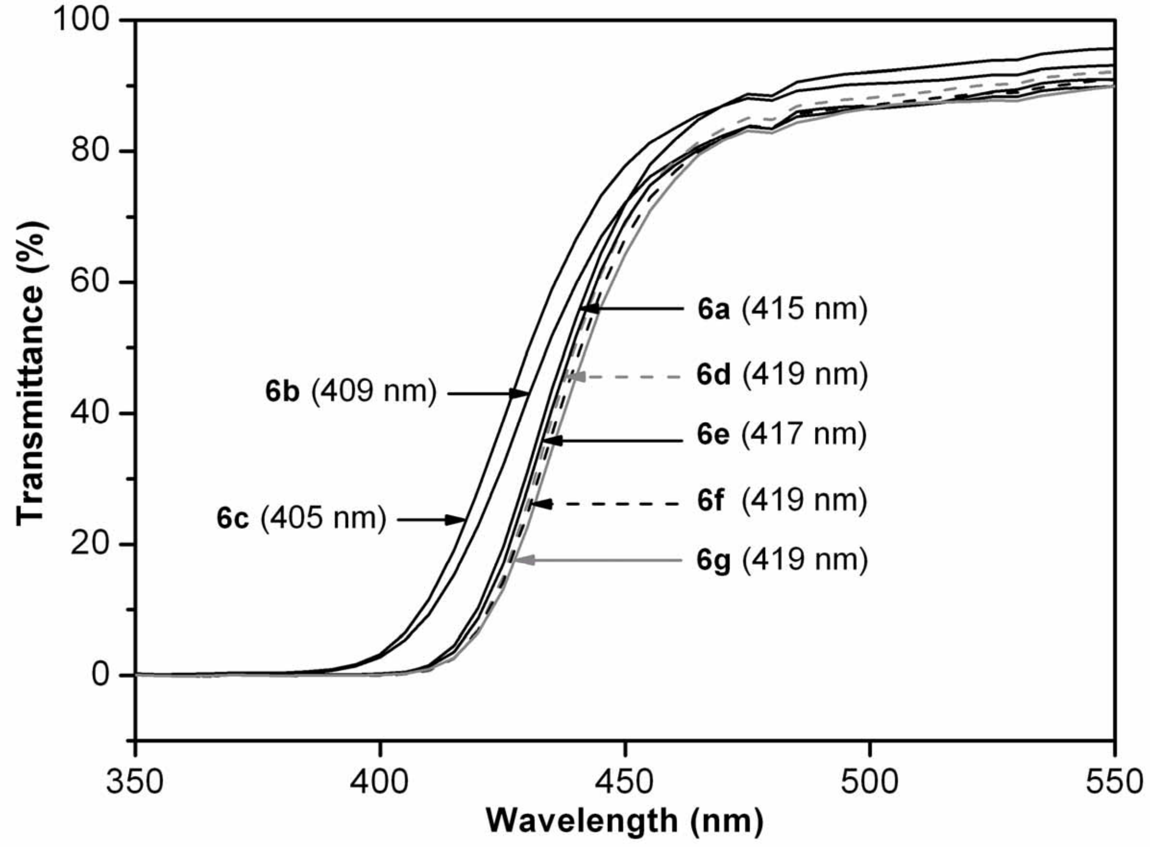
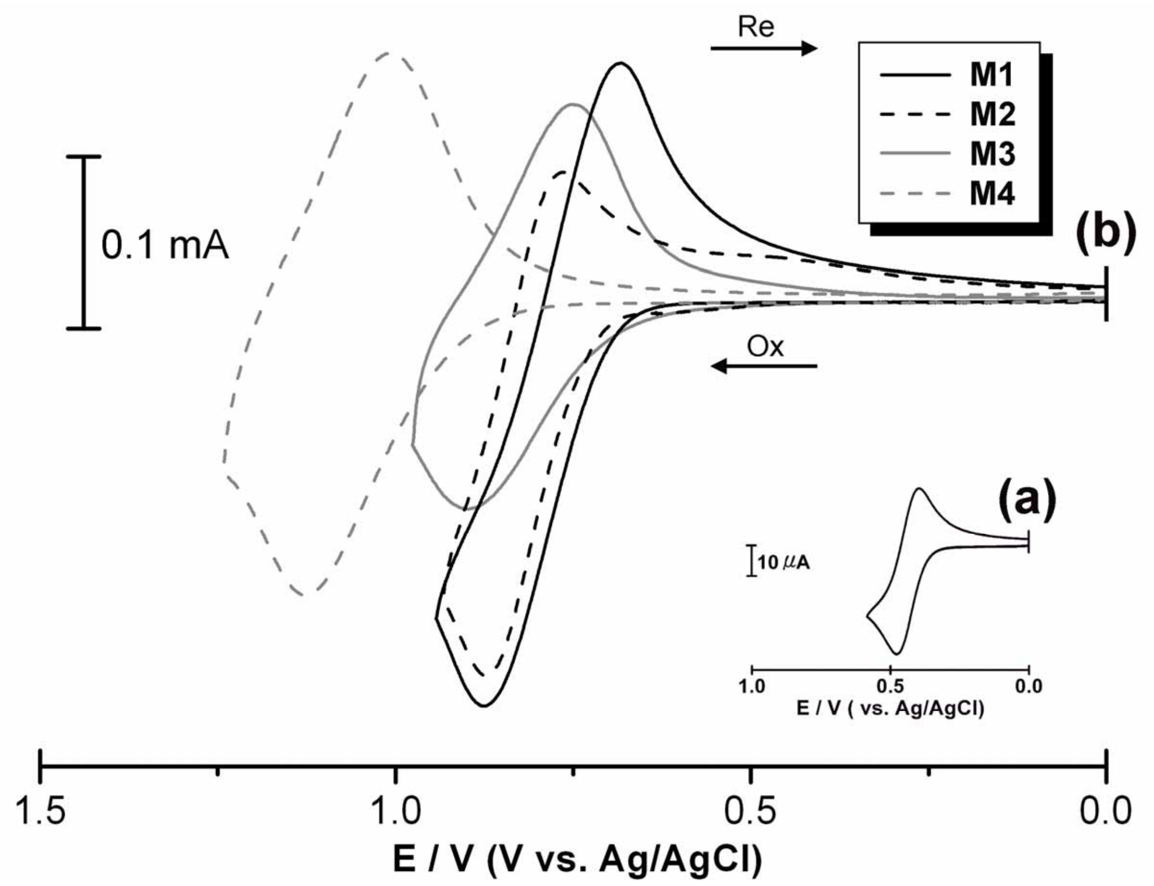
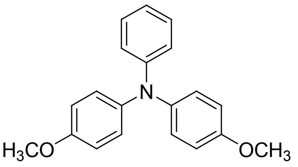
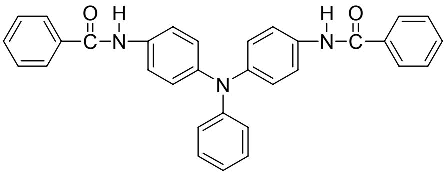


Fig. S10 UV-vis transmission spectra of polyamide **6** series films (thickness: 1-3 μm).

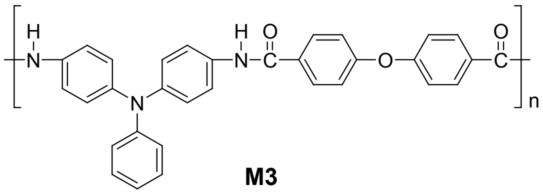




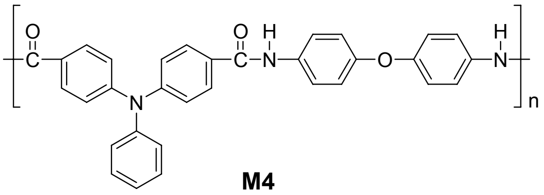
M1



M2



M3



M4

Fig. S11 Cyclic voltammograms of (a) ferrocene (b) model compounds **M1, M2** and polyamides **M3** and **M4** in CH_3CN containing 0.1 M TBAP at scan rate = 0.05 V/s.