# Supporting Information

## Enhanced Near-Infrared Electrochromism in Triphenylamine-based Aramids Bearing Phenothiazine Redox Centers

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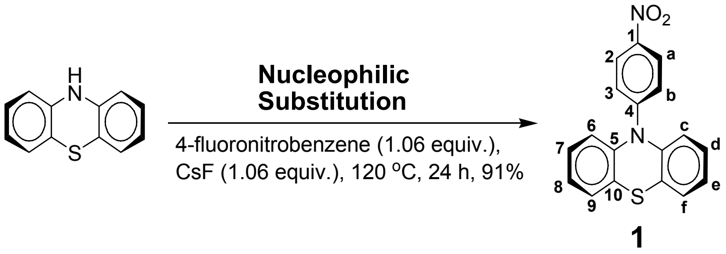
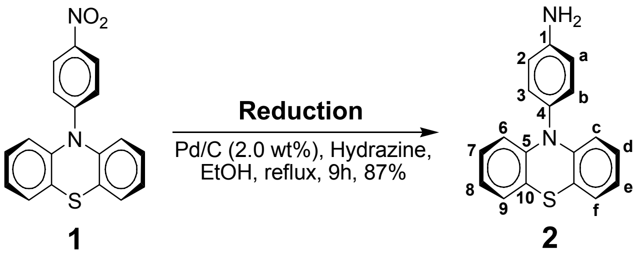
### List of Contents for Supplementary Material:

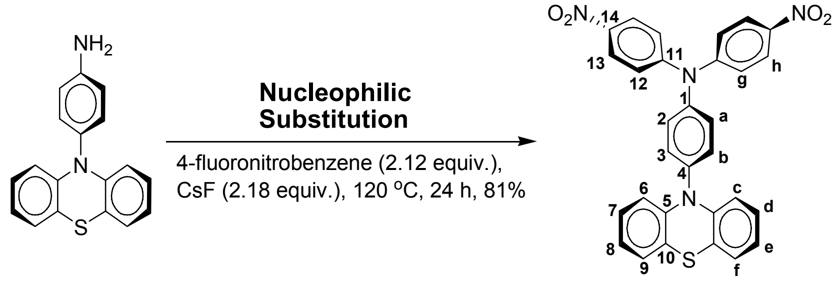
**Monomer synthesis.**



***N*-(4-Nitrophenyl)phenothiazine (1).** To a solution of 36.92 g (0.18 mol) of phenothiazine and 27.31 g (0.19 mol) of 4-fluoronitrobenzene in 70 mL of dried dimethyl sulfoxide (DMSO), 29.57 g (0.19 mol) of dried cesium fluoride (CsF) was added with stirring all at once, and the mixture was heated at 120 °C for 24 h under a nitrogen atmosphere. The mixture was slowly poured into 600 mL of stirred methanol, and the precipitated yellow crystals was collected by filtration and washed thoroughly with methanol/water. The product was filtered to afford 53.41 g (91 % in yield) of yellow crystals with a mp of 162-164 °C (measured by DSC at 10 °C/min) (lit.[SR1] 157 °C). FT-IR (KBr): 1337, 1578 cm$^{-1}$ (-$NO_2$ stretch). $^1$H NMR (DMSO-$d_6$, δ, ppm): 7.02 (d, 2H, $H_b$), 7.32 (t, 2H, $H_e$), 7.45 (t, 2H, $H_d$), 7.54 (d, 2H, $H_c$), 7.60 (d, 2H, $H_f$), 8.08 (d, 2H, $H_a$). $^{13}$C NMR (DMSO-$d_6$, δ, ppm): 114.4 ($C^{10}$), 125.9 ($C^6$), 127.1 ($C^2$), 127.2 ($C^3$), 128.2 ($C^8$), 129.2 ($C^7$), 133.3 ($C^9$), 140.1 ($C^5$), 140.6 ($C^4$), 150.7 ($C^1$). Anal. Calcd (%) for $C_{18}H_{12}N_2O_2S$ (320.37): C, 67.48; H, 3.78; N, 8.74. Found: C, 67.49; H, 3.65; N, 8.72. FAB-MS $[M]^+$: Calcd., 320.1; Found 320.1.

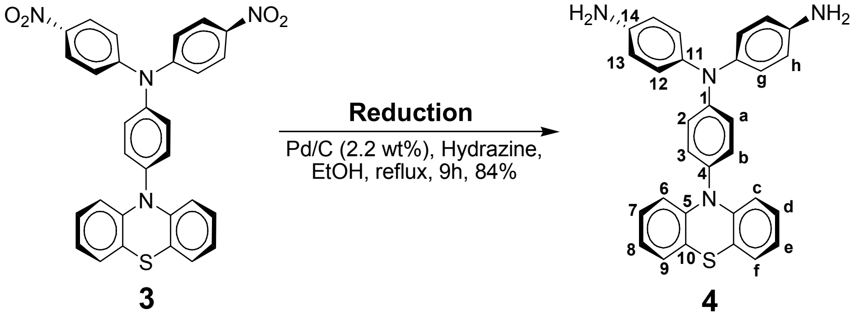


***N*-(4-Aminophenyl)phenothiazine (2).** In a 500-mL three-neck round-bottomed flask equipped with a stirring bar under nitrogen atmosphere, 7.99 g (24.94 mmol) of nitro compound **1** and 0.16 g of 10 % Pd/C were dissolved/suspended in 240 mL of ethanol. The suspension solution was heated to reflux, and 4 mL of hydrazine monohydrate was added slowly to the mixture. After the solution was stirred at reflux temperature for 9 h, the solution was filtered to remove Pd/C, and the filtrate was cooled to precipitate transparent crystals. The product was collected by filtration and dried *in vacuo* at 80 $^{o}$C to give 6.31 g (87 % in yield) of transparent crystals with a mp of 182-183 $^{o}$C (by DSC) (lit.[SR1] 132-133 $^{o}$C). FT-IR (KBr): 3342-3475 cm$^{-1}$ (N-H stretch). $^{1}$H NMR (DMSO-$d_6$, δ, ppm): 5.44 (s, 2H, $NH_2$), 6.27 (d, 2H, $H_a$), 6.75 (t, 2H, $H_e$), 6.82 (t, 2H, $H_d$), 6.91 (d, 2H, $H_c$), 6.96 (d, 2H, $H_f$), 7.04 (d, 2H, $H_b$). $^{13}$C NMR (DMSO-$d_6$, δ, ppm): 115.7 ($C^2$), 115.8 ($C^3$), 118.8 ($C^{10}$), 122.3 ($C^6$), 126.5 ($C^8$), 127.2 ($C^7$), 128.1 ($C^4$), 131.3 ($C^9$), 144.7 ($C^5$), 148.8 ($C^1$). Anal. Calcd (%) for $C_{18}H_{14}N_2S$ (290.38): C, 74.45; H, 4.86; N, 9.65. Found: C, 74.52 ; H, 4.79; N, 9.59. FAB-MS $[M]^+$: Calcd., 290.1; Found 290.2.



**2** **3**

**4,4’-Dinitro-4”-*N*-phenothiazinyltriphenylamine (3).** To a solution of 2.08 g (7.15 mmol) of compound **2** and 2.16 g (15.14 mmol) of 4-fluoronitrobenzene in 15 mL of dried DMSO, 2.39 g (15.58 mol) of dried cesium fluoride was added with stirring all at once, and the mixture was heated at 120 $^{o}$C for 24 h under nitrogen atmosphere. The mixture was poured into 300 mL of stirred methanol slowly, and the precipitated red powder was collected by filtration and reprecipitated by DMF/methanol. The product was filtered to afford 3.10 g (81 % in yield) of orange crystals with a mp of 215-216 °C (by DSC). FT-IR (KBr): 1341, 1582 $cm^{-1}$ ($NO_2$ stretch). $^1H$ NMR (DMSO-$d_6$, δ, ppm): 6.46 (d, 2H, $H_c$), 6.92 (t, 2H, $H_e$), 7.02 (t, 2H, $H_d$), 7.12 (d, 2H, $H_f$), 7.31 (d, 4H, $H_g$), 7.42 (s, 4H, $H_a$ + $H_b$), 8.20 (d, 4H, $H_h$). $^{13}C$ NMR (DMSO-$d_6$, δ, ppm): 117.8 ($C^6$), 121.3 ($C^{10}$), 123.2 ($C^{12}$), 123.5 ($C^8$), 125.8 ($C^{13}$), 127.1 ($C^9$), 127.6 ($C^7$), 129.1 ($C^2$), 130.6 ($C^3$), 139.2 ($C^4$), 142.5 ($C^5$), 143.4 ($C^{11}$), 143.5 ($C^1$), 151.7 ($C^{14}$). Anal. Calcd (%) for $C_{30}H_{20}N_4O_4S$ (532.57): C, 67.66; H, 3.79; N, 10.52. Found: C, 67.69; H, 3.68; N, 10.42. FAB-MS $[M]^+$: Calcd., 532.1; Found 532.1.



**4,4'-Diamino-4"-*N*-phenothiazinyltriphenylamine (4).** In a 100-mL three-neck round-bottomed flask equipped with a stirring bar under nitrogen atmosphere, 0.32 g (0.59 mmol) of dinitro compound **3** and 0.07 g of 10 % Pd/C were dissolved/suspended in 12 mL of ethanol. The suspension solution was heated to reflux, and 1 mL of hydrazine monohydrate was added slowly to the mixture. After the solution was stirred at reflux temperature for 9 h, the solution was filtered to remove Pd/C, and the filtrate was cooled to precipitate white crystals. The product was collected by filtration and dried *in vacuo* at 80 °C to give 0.24 g (84 % in yield) of white crystals with a mp of 183-185 °C (by DSC). FT-IR (KBr): 3215, 3338 $cm^{-1}$ (N-H stretch). $^1H$ NMR (DMSO-$d_6$, δ, ppm): 5.06 (s, 4H, -$NH_2$), 6.24 (d, 2H, $H_c$), 6.18 (d, 4H, $H_h$), 6.76-6.79 (m, 4H, $H_a$ + $H_e$), 6.88 (t, 2H, $H_d$), 6.97 (d, 6H, $H_f$ + $H_g$), 7.03 (d, 2H, $H_b$). $^{13}C$ NMR (DMSO-$d_6$, δ, ppm): 115.1 ($C^{13}$), 115.8 ($C^6$), 117.0 ($C^8$), 118.8 ($C^{10}$), 122.4 ($C^2$), 126.6 ($C^9$), 127.3 ($C^7$), 128.2 ($C^{12}$), 129.0 ($C^4$), 131.0 ($C^3$), 135.4 ($C^{11}$), 144.5 ($C^5$), 146.4 ($C^{14}$), 149.7 ($C^1$). Anal. Calcd (%) for $C_{30}H_{24}N_4S$ (472.60): C, 76.24; H, 5.12; N, 11.85. Found: C, 75.95; H, 5.15; N, 11.52. FAB-MS $[M]^+$: Calcd., 472.2; Found 472.2.

**Reference**

SR1. Gilman, H.; Shirley, D. A. *J. Am. Chem. Soc.* **1944**, *66*, 888.

**Table S1.** Inherent Viscosity[a] and Molecular Weights[b] of Polyamides

| polymer | $\eta_{inh}$ (dL/g) | $M_w$ | $M_n$ | PDI[c] | DP[d] |
|---|---|---|---|---|---|
| **Ia** | 0.36 | 47100 | 31300 | 1.50 | 51 |
| **Ib** | 0.29 | 38500 | 25300 | 1.52 | 42 |
| **Ic** | 0.35 | 160900 | 79400 | 2.03 | 114 |
| **Id** | 0.29 | 51700 | 36700 | 1.41 | 44 |

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

[b] Calibrated with polystyrene standards, using DMF as the eluent at a constant flow rate of 1 mL/min at 70 °C.

[c] Polydispersity Index ($M_w/M_n$).

[d] Degree of Polymerization.

**Table S2.** Solubility Behavior of Polyamides

| Code | Solubility in various Solvent[a] | | | | | | |
|---|---|---|---|---|---|---|---|
| | NMP | DMAc | DMF | DMSO | *m*-Cresol | THF | $CHCl_3$ |
| **Ia** | + + | + + | + + | + + | + + | + - | + - |
| **Ib** | + + | + + | + + | + + | + + | + - | + - |
| **Ic** | + + | + + | + + | + | + + | + - | + - |
| **Id** | + + | + + | + + | + + | + + | + + | + - |

[a] The solubility was determined with a 10 mg sample in 1 mL of a solvent. + +, soluble at room temperature; +, soluble on heating; + -, partially soluble or swelling; -, insoluble even on heating.

**Table S3.** Thermal Properties[a] of Polyamides

| Code | $T_g$ (°C)[b] | $T_s$ (°C)[c] | $T_d^5$ (°C)[d] |  | $T_d^{10}$ (°C)[e] |  | Char Yield (wt %)[f] |
|---|---|---|---|---|---|---|---|
|  |  |  | $N_2$ | Air | $N_2$ | Air |  |
| **Ia** | 255 | 253 | 450 | 435 | 500 | 485 | 67 |
| **Ib** | 274 | 275 | 510 | 510 | 585 | 570 | 77 |
| **Ic** | 277 | 274 | 490 | 485 | 570 | 565 | 73 |
| **Id** | 276 | 274 | 510 | 515 | 575 | 560 | 71 |

[a] The polymer film samples were heated at 300 °C for 1 h prior to all the thermal analyses.

[b] Midpoint temperature of baseline shift on the second DSC heating trace (rate: 20 °C/min) of the sample after quenching from 400 °C to 50 °C (rate: 200 °C /min) in nitrogen.

[c] Softening temperature measured by TMA with a constant applied load of 50 mN at a heating rate of 10 °C/min.

[d] Temperature at which 5 % weight loss occurred, recorded via TGA at a heating rate of 20 °C/min and a gas-flow rate of 20 $cm^3$/min.

[e] Temperature at which 10 % weight loss occurred.

[f] Residual weight percentage at 800 °C under nitrogen flow.

**Table S4.** Electrochemical Properties of Model Compounds **M1**, **M2**, and **M3**

| Code | Oxidation potential (V) (vs. Ag/AgCl in $CH_3CN$) | |
|---|---|---|
| | $E_{1/2}$[a] | $E_{onset}$ |
| **M1** | 0.79 | 0.73 |
| **M2** | 0.82 | 0.75 |
| **M3** | -[b] | 0.96 |

[a] $E_{1/2}$ (Average potential of the redox couple peaks).

[b] The oxidation redox couples is irreversible.

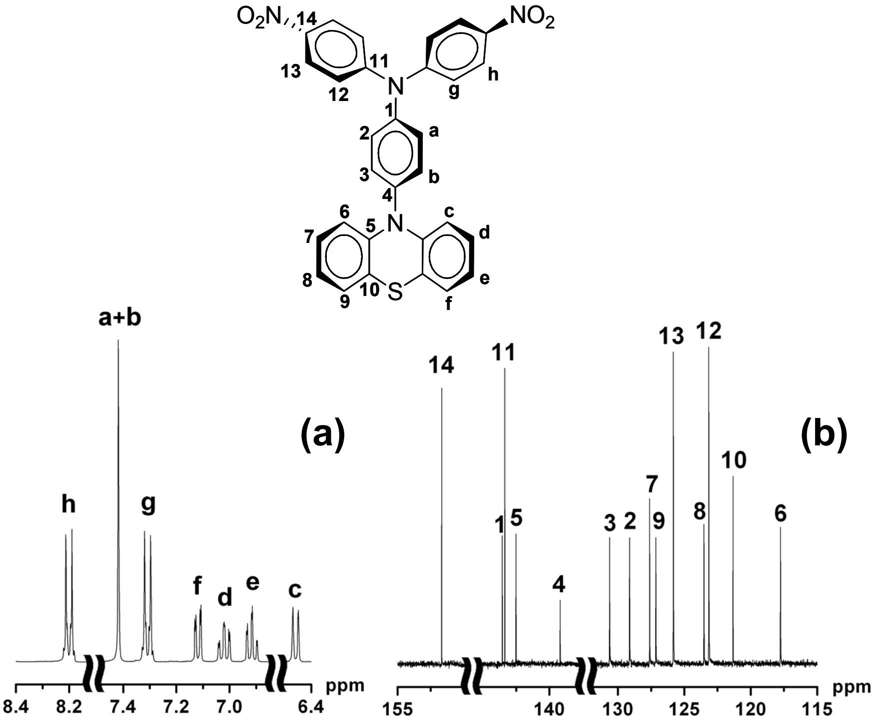


**Figure S1.** (a) $^{1}$H NMR and (b) $^{13}$C NMR spectrum of dinitro compound **3** in DMSO-$d_6$

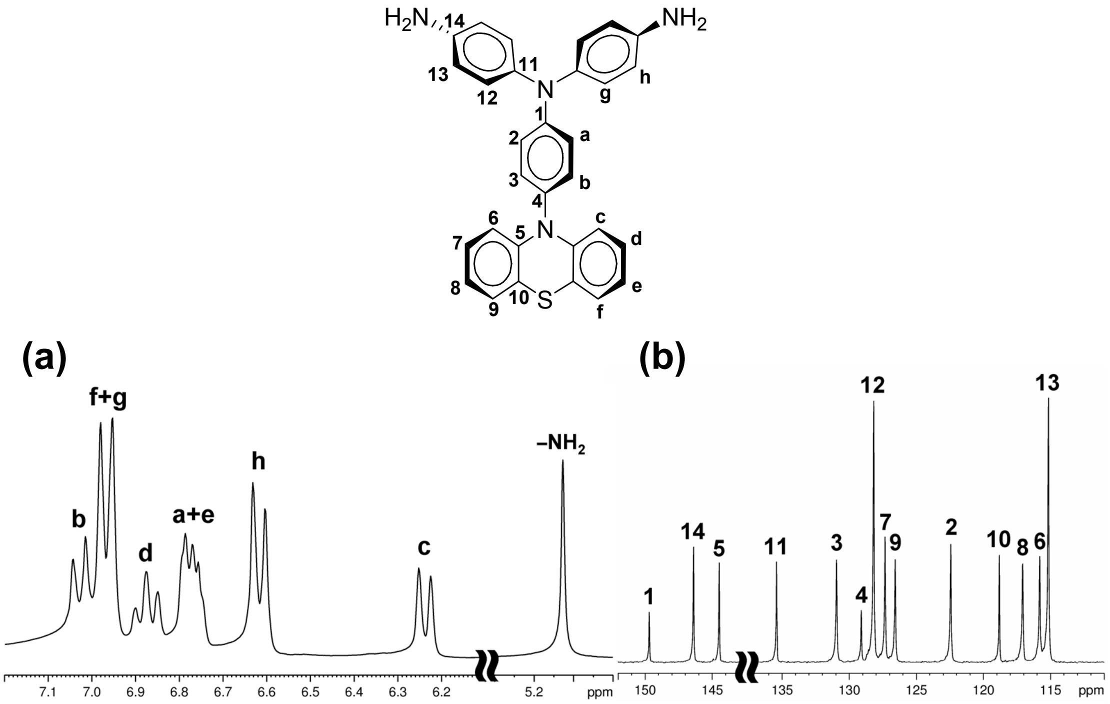


**Figure S2.** (a) $^{1}$H NMR and (b) $^{13}$C NMR spectrum of diamine monomer **4** in DMSO-$d_6$

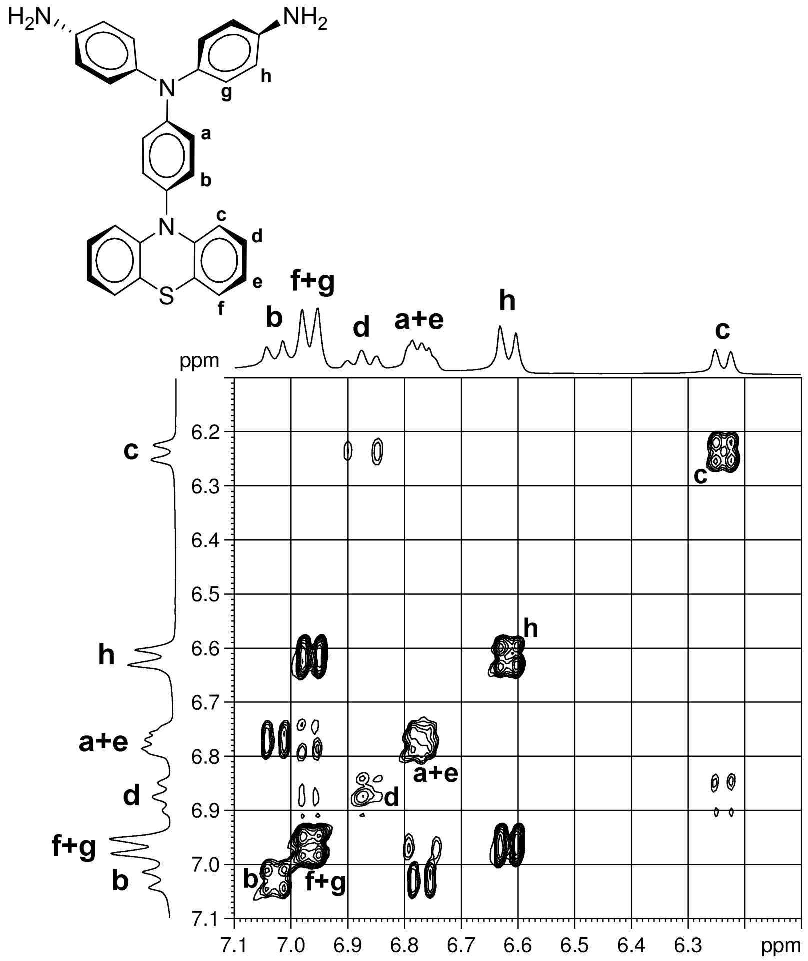


**Figure S3.** H-H COSY spectrum of diamine monomer **4** in DMSO-$d_6$.

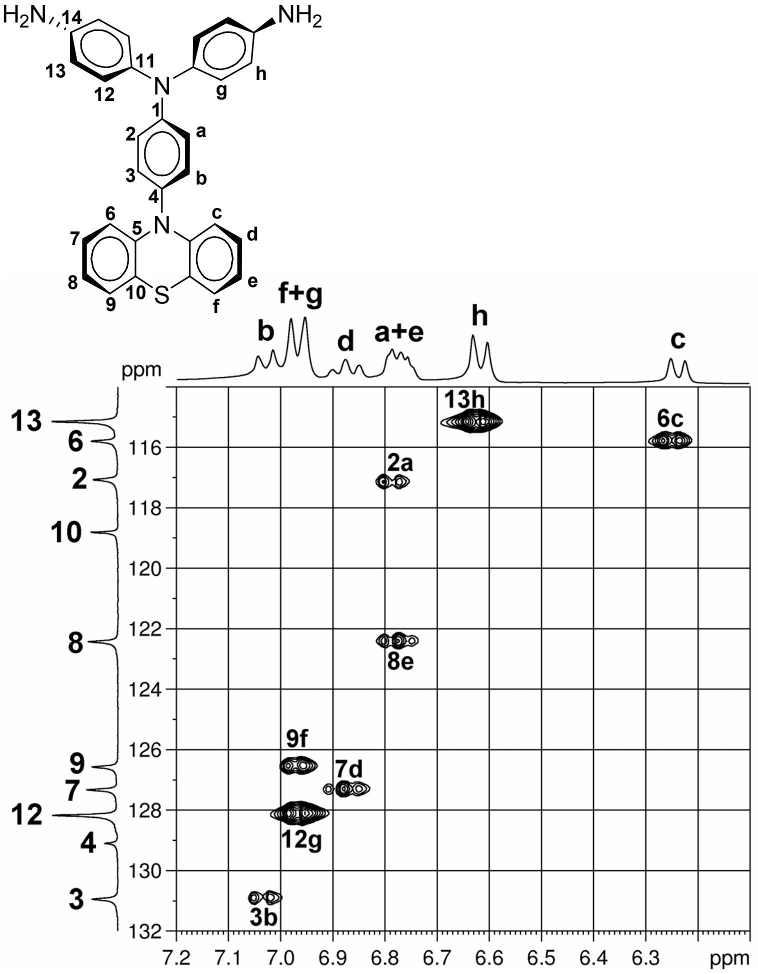


**Figure S4.** C-H HMQC spectrum of diamine monomer **4** in DMSO-$d_6$.

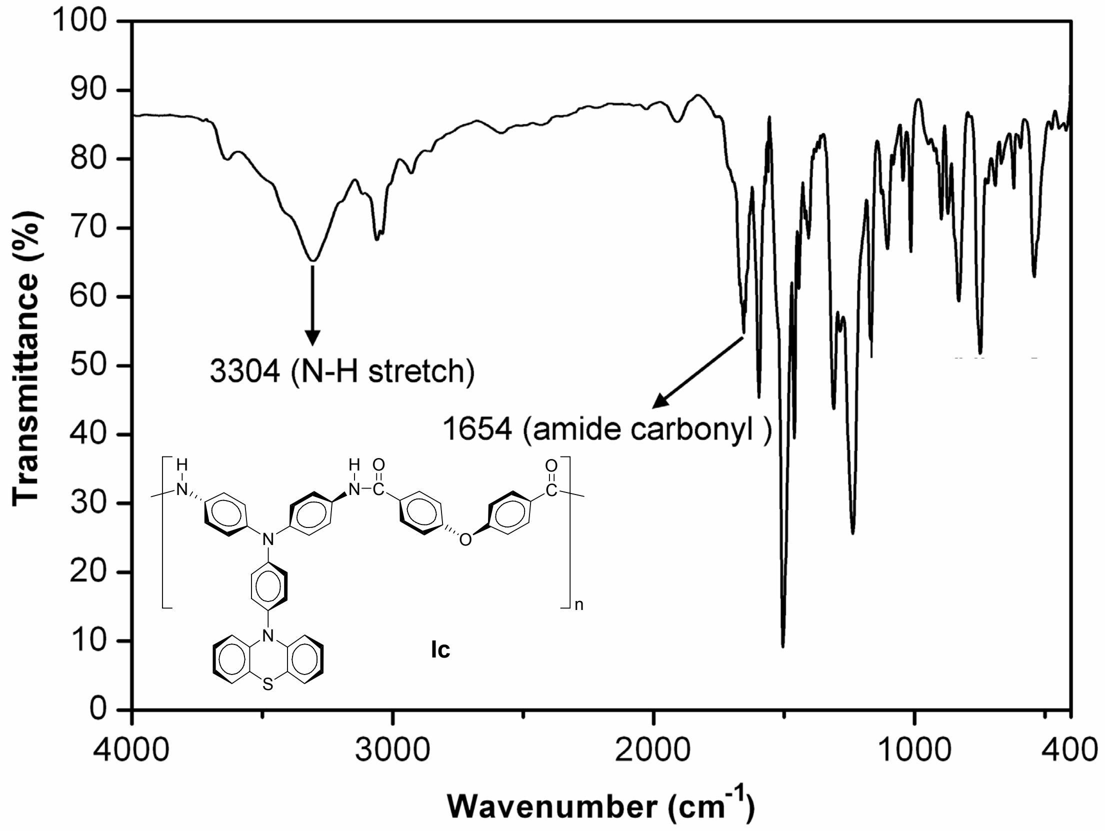


**Figure S5.** IR spectrum of polyamide **Ic** film.

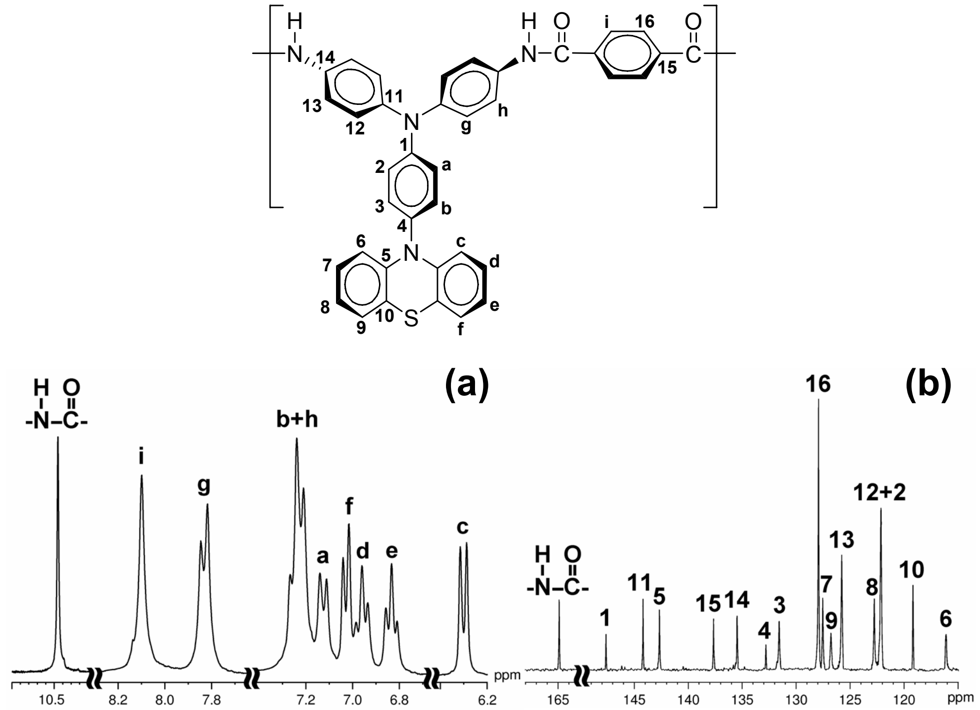


**Figure S6.** (a) $^{1}$H NMR and (b) $^{13}$C NMR spectrum of polyamide **Ib** in DMSO-$d_6$.

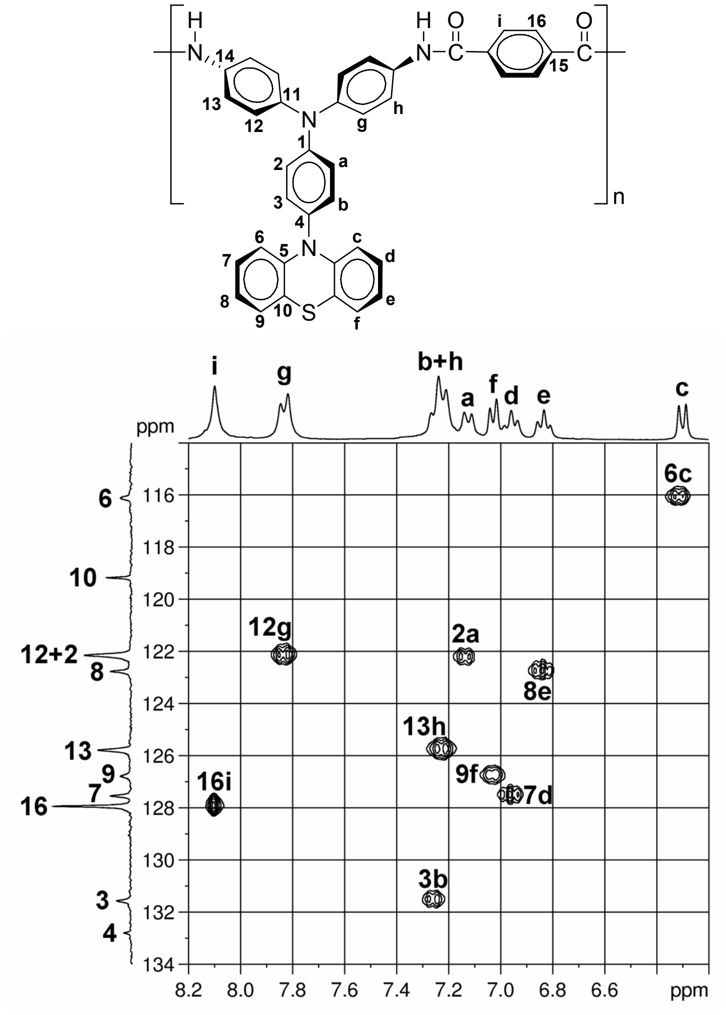


**Figure S7.** C-H HMQC spectrum of polyamide **Ib** in DMSO-$d_6$.

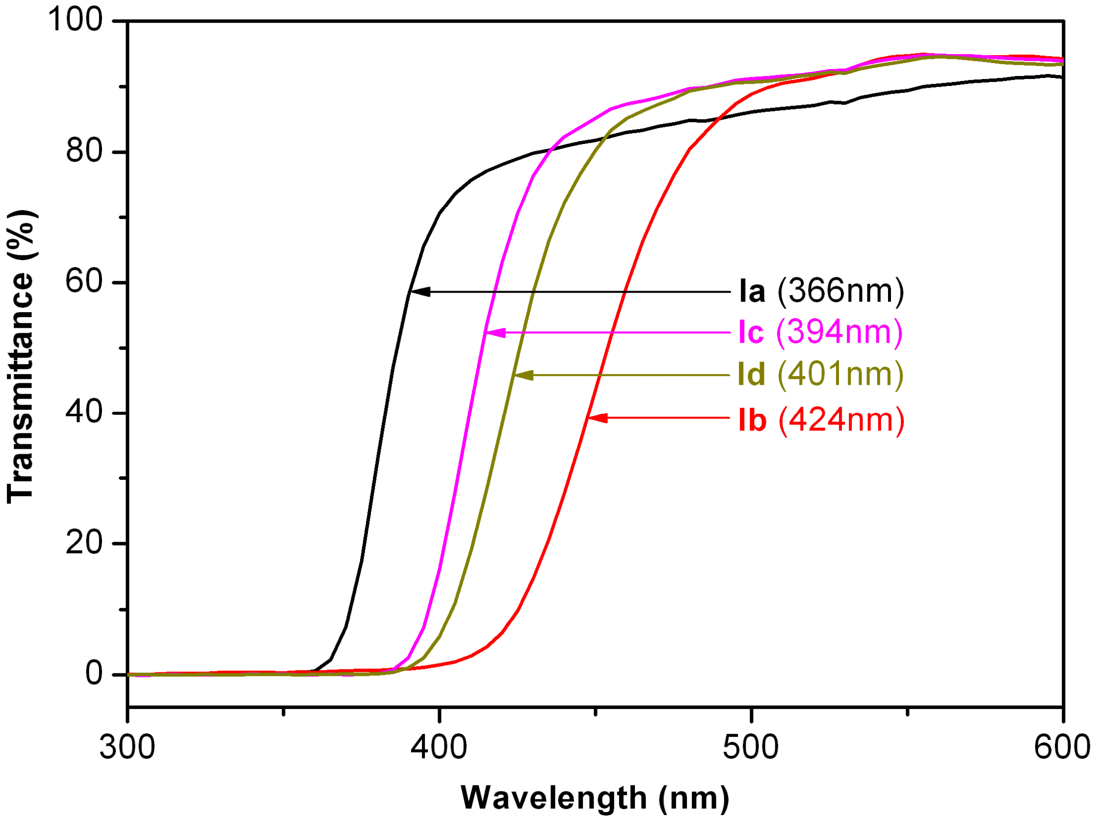


**Figure S8.** UV-visible transmission spectra of the polyamide **I** films (thickness ~5 μm)

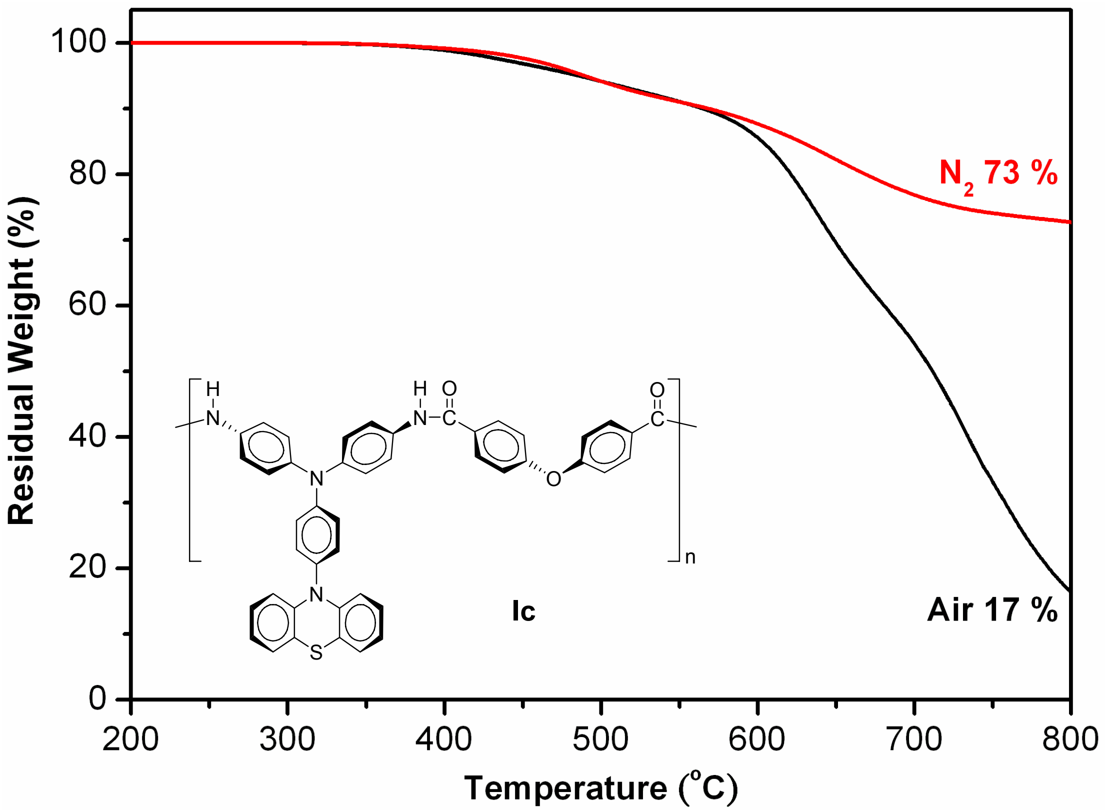


**Figure S9.** TGA thermograms of polyamide **Ic** at a scan rate of 20 °C/min.

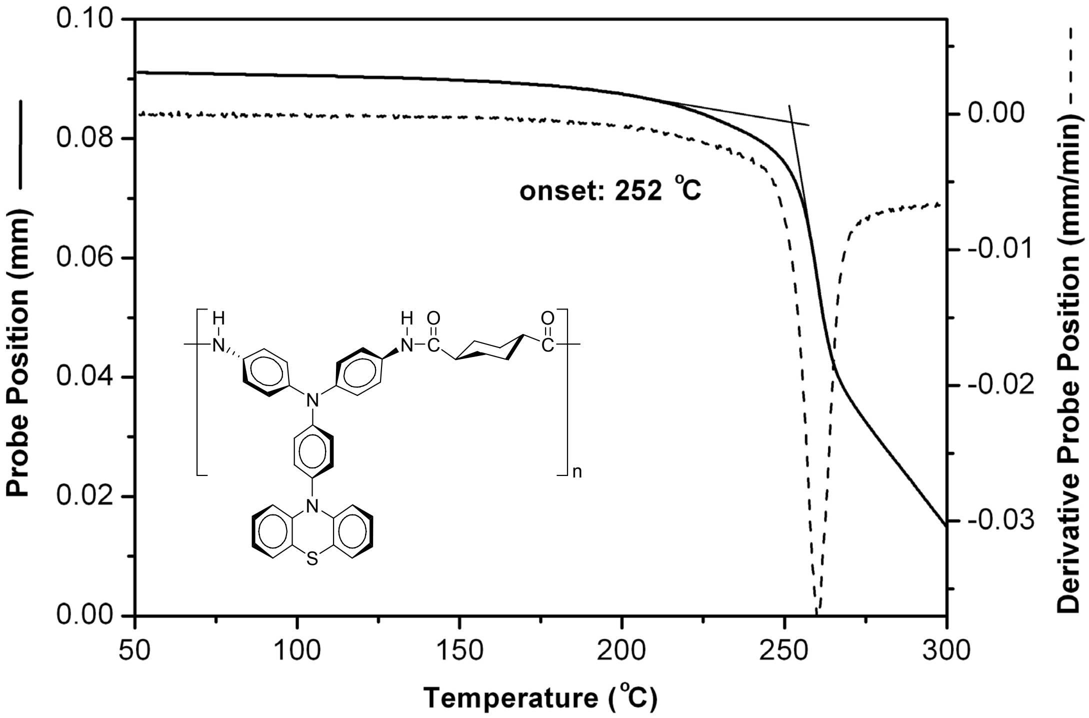


**Figure S10.** TMA curve of polyamide **Ia** with a heating rate of 10 °C/min.

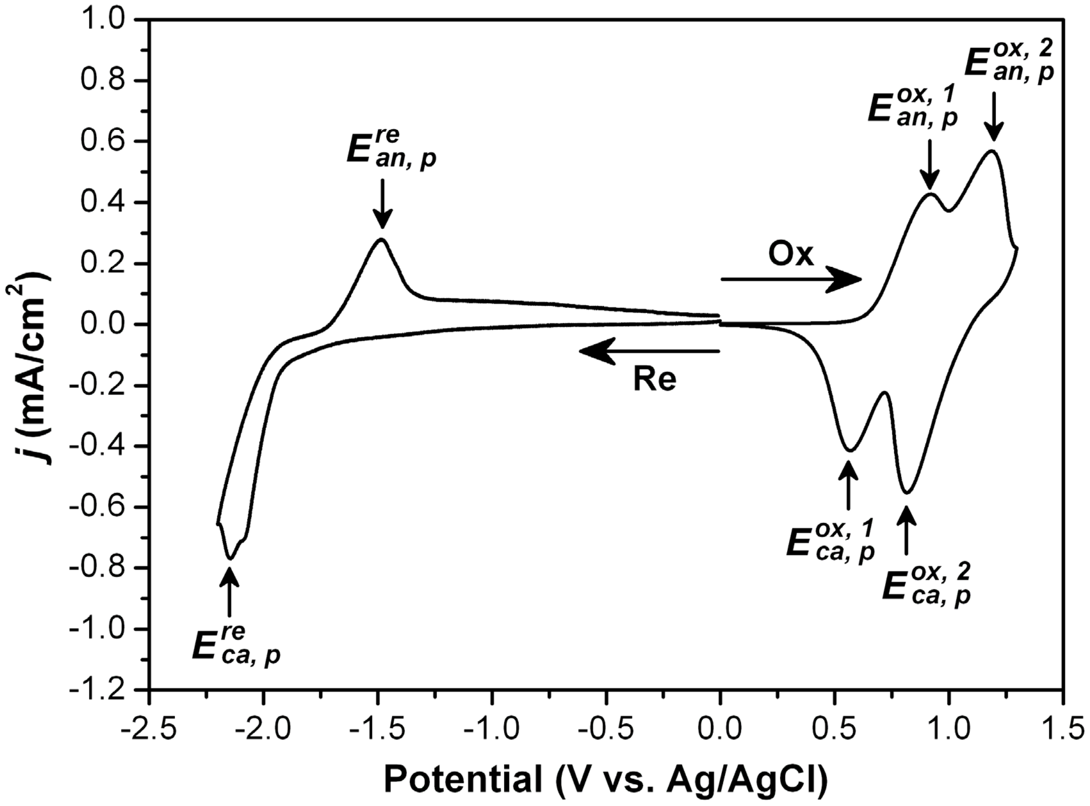


**Figure S11.** Cyclic voltammograms of polyamide **Ic** film on an ITO-coated glass substrate in $CH_3CN$ (oxidation) and DMF (reduction) solutions containing 0.1 M TBAP at scan rate of 50 and 200 mV/s, respectively.

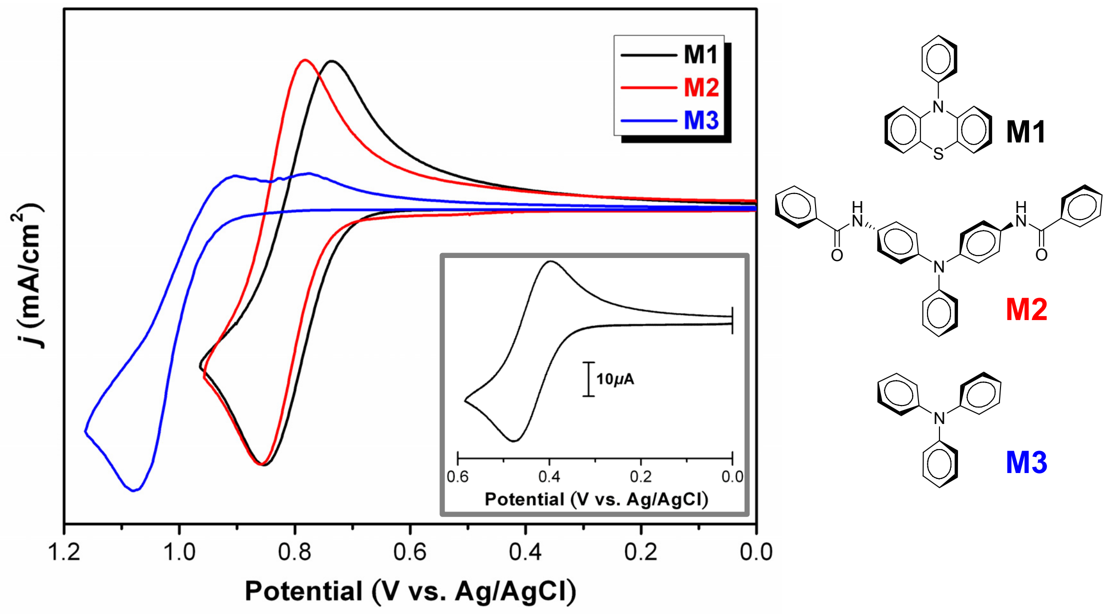


**Figure S12.** Cyclic voltammetric diagrams of model compounds **M1**, **M2**, **M3**, and ferrocene (inset) in $CH_3CN$ solutions containing 0.1 M TBAP at a scan rate of 50 mV/s.