

Supporting Information

Novel Triarylamine-based Aromatic Polyamides Bearing Secondary amine: Synthesis and Redox Potential Inversion Characteristics by Pyridines

By *Hung-Ju Yen*,[†] *Jhe-Huang Lin*,[†] *Yuhlong Oliver Su*,* *Guey-Sheng Liou**

[†] Institute of Polymer Science and Engineering, National Taiwan University

§ Department of Applied Chemistry, National Chi Nan University

E-mail: yosu@ncnu.edu.tw (Prof. Y. O. Su); gслиou@ntu.edu.tw (Prof. G. S. Liou)

[†]These authors contributed equally.

List of Contents for Supplementary Material:

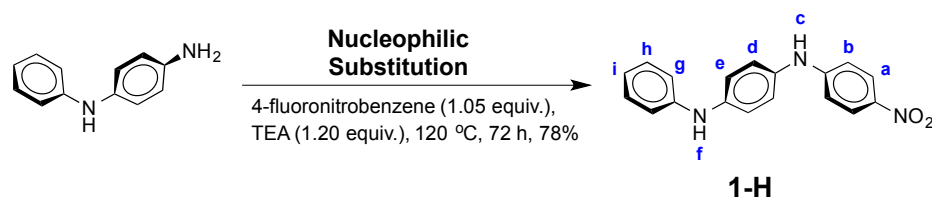
Experimental Section	<i>SI-3</i>
Measurements	<i>SI-12</i>
Figure S1. FT-IR spectra of compounds (a) 2-H and (b) 3-H	<i>SI-13</i>
Figure S2. FT-IR spectra of compounds (a) 2-OMe and (b) 3-OMe	<i>SI-14</i>
Figure S3. FT-IR spectra of model compounds (a) M-H and (b) M-OMe	<i>SI-15</i>
Figure S4. ¹ H-NMR spectra of 1-H in DMSO- <i>d</i> ₆	<i>SI-16</i>
Figure S5. ¹ H-NMR spectra of 1-OMe in DMSO- <i>d</i> ₆	<i>SI-16</i>
Figure S6. ¹ H-NMR spectra and ¹³ C-NMR spectra of 2-H in DMSO- <i>d</i> ₆	<i>SI-17</i>
Figure S7. H-H COSY and C-H HSQC spectra of 2-H in DMSO- <i>d</i> ₆	<i>SI-17</i>
Figure S8. ¹ H-NMR spectra and ¹³ C-NMR spectra of 2-OMe in DMSO- <i>d</i> ₆	<i>SI-18</i>
Figure S9. H-H COSY and C-H HSQC spectra of 2-OMe in DMSO- <i>d</i> ₆	<i>SI-18</i>
Figure S10. ¹ H-NMR spectra and ¹³ C-NMR spectra of 3-H in DMSO- <i>d</i> ₆	<i>SI-19</i>
Figure S11. H-H COSY and C-H HSQC spectra of 3-H in DMSO- <i>d</i> ₆	<i>SI-19</i>
Figure S12. ¹ H-NMR spectra and ¹³ C-NMR spectra of 3-OMe in DMSO- <i>d</i> ₆	<i>SI-20</i>
Figure S13. H-H COSY and C-H HSQC spectra of 3-OMe in DMSO- <i>d</i> ₆	<i>SI-20</i>
Figure S14. ¹ H-NMR spectra of model compounds M-H and M-OMe in DMSO- <i>d</i> ₆	<i>SI-21</i>
Figure S15. IR spectra of polyamides (a) PA-H (b) PA-OMe	<i>SI-21</i>
Figure S16. ¹ H NMR of polyamide PA-H in DMSO- <i>d</i> ₆	<i>SI-22</i>
Figure S17. TGA thermograms of polyamides PA-H and PA-OMe	<i>SI-23</i>
Figure S18. TMA curves of polyamides PA-H and PA-OMe	<i>SI-23</i>
Figure S19. Cyclic voltammograms of M-OMe with equal molar of aniline and methylamine	<i>SI-24</i>
Figure S20. Absorption spectra change of 10 μmol M-OMe in 0.1 M TBAP/CH ₃ CN with various amount of Me ₃ Py [pK _a =7.48] at 0.45 (V vs. Ag/AgCl).....	<i>SI-24</i>
Table S1. Inherent Viscosity and Solubility Behavior of Polyamides.....	<i>SI-25</i>
Table S2. Thermal Properties of Polyamides.....	<i>SI-25</i>

Materials

N-(4-Aminophenyl)-*N*-(4'-methoxyphenyl)amine¹⁷ was synthesized from the hydrogenation of *N*-(4-methoxyphenyl)-*N*-(4'-nitrophenyl)amine¹⁶ according to the previously reported procedure. Commercially obtained anhydrous calcium chloride (CaCl₂) was dried under vacuum at 180 °C for 8 h. Tetrabutylammonium perchlorate (TBAP) (ACROS) was recrystallized twice by ethyl acetate under nitrogen atmosphere and then dried in *vacuo* prior to use. All other reagents were used as received from commercial sources.

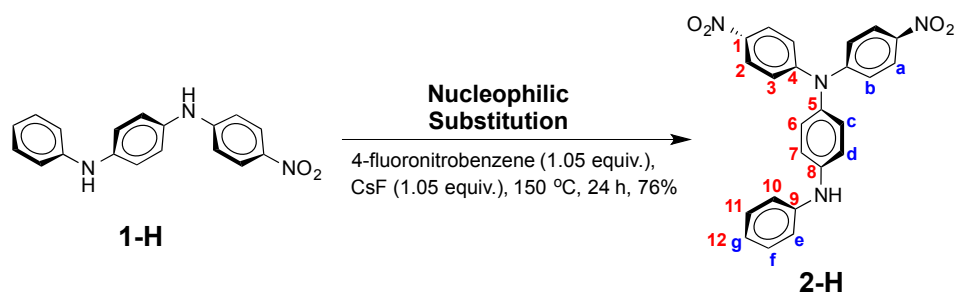
Monomer Synthesis

N-(4-Nitrophenyl)-*N'*-phenyl-1,4-phenylenediamine (1-H)



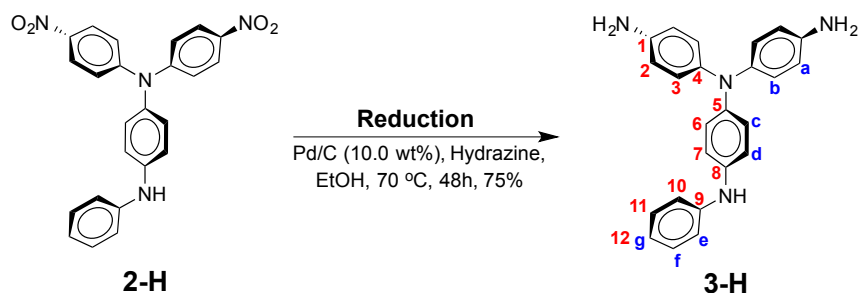
N-(4-Nitrophenyl)-*N'*-phenyl-1,4-phenylenediamine was prepared from the triethylamine-mediated aromatic nucleophilic mono-substitution reaction of *N*-phenyl-1,4-phenylenediamine with 4-fluoronitrobenzene in DMSO according to the reported procedure (mp 139-140 °C; lit.¹⁸ 132–134 °C). IR (KBr): 3338-3326 cm⁻¹ (secondary N-H stretch), 1599 and 1291 cm⁻¹ (-NO₂ stretch). ¹H NMR (400 MHz, DMSO-*d*₆, δ, ppm): 9.09 (s, 1H), 8.15 (s, 1H), 8.04–8.02 (m, 2H), 7.23 (t, 2H), 7.14–7.08 (m, 4H), 7.06–7.04 (m, 2H), 6.91–6.89 (m, 2H), 6.79 (t, 1H).

N, N-Bis(4-nitrophenyl)-N'-phenylbenzene-1,4-diamine (2-H)



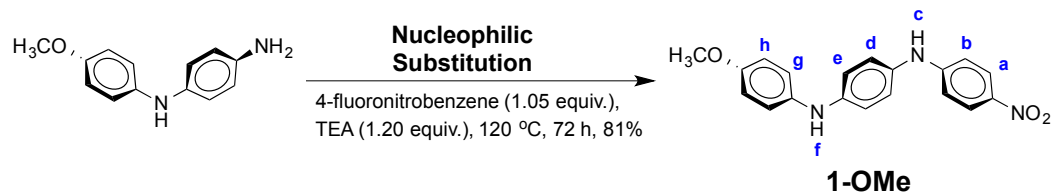
A mixture of 3.19 g (21.0 mmol) of cesium fluoride (CsF) was added to 30 mL of DMSO at room temperature. To the mixture 6.10 g (20.0 mmol) of compound **1-H** and 2.96 g (21.0 mmol) of 4-fluoronitrobenzene were added in sequence. The mixture was stirred at 150 °C for 24 h under nitrogen atmosphere. After the reaction, the mixture was poured into 300 mL of stirred methanol slowly, and precipitated dark red powder was collected by filtration and washed thoroughly with water. Reprecipitation from DMF/MeOH gives dinitro compound **2-H** as dark red powder with 76% in yield. m.p.: 206-208 °C measured by DSC at 5 °C/min. IR (KBr): 3369 cm^{-1} (secondary N-H stretch), 1585 and 1305 cm^{-1} ($-\text{NO}_2$ stretch). ^1H NMR (500 MHz, $\text{DMSO}-d_6$, δ , ppm): 8.42 (s, 1H, -NH), 8.18-8.15 (d, 4H, H_a), 7.28-7.25 (t, 2H, H_f), 7.21-7.19 (d, 4H, H_b), 7.17-7.10 (m, 6H, $\text{H}_d + \text{H}_e + \text{H}_c$), 6.90-6.87 (t, 1H, H_g). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$, δ , ppm): 151.73 (C^4), 143.09 (C^9), 142.50 (C^5), 141.57 (C^1), 135.24 (C^8), 129.22 (C^{11}), 128.83 (C^6), 125.27 (C^2), 121.66 (C^3), 120.56 (C^{12}), 117.75 (C^{10}), 117.35 (C^7). Anal. Calcd. (%) for $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_4$ (426.42): C, 67.60 %; H, 4.25 %; N, 13.14 %. Found: C, 67.46 %; H, 4.18 %; N, 13.07 %.

N, N-Bis(4-aminophenyl)-N'-phenylbenzene-1,4-diamine (3-H)



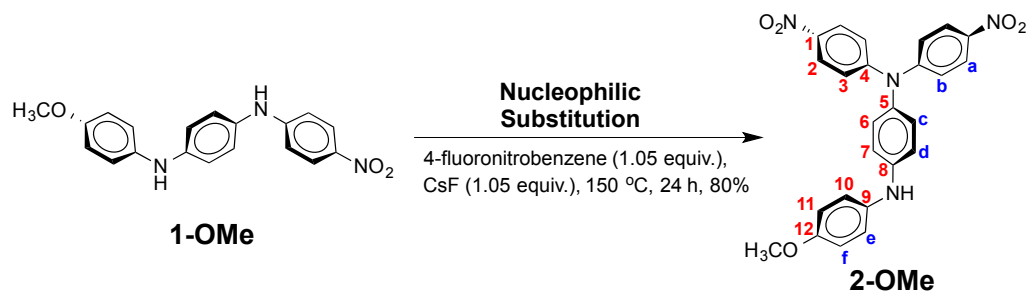
In a 100 mL two-neck round-bottomed flask equipped with a stirring bar under nitrogen atmosphere, 4.26 g (10.0 mmol) of dinitro compound **2-H** and 0.42 g of 10 % Pd/C were dispersed/suspended in 60 mL of ethanol. The suspension solution was heated to reflux, and 5 mL of hydrazine monohydrate was added slowly to the mixture. After a further 48 h of reflux, the solution was filtered to remove Pd/C, and the filtrate was cooled to precipitate. The product was collected by filtration and dried *in vacuo* at 80 °C to give 2.75 g (75 % in yield) of light gray powder. m.p.: 215-216 °C measured by DSC at 5 °C/min. IR (KBr): 3389-3367 cm⁻¹ (primary and secondary N-H stretch). ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm): 7.51 (s, 1H, -NH), 7.15-7.12 (d, 2H, H_f), 6.92-6.90 (m, 4H, H_e + H_d), 6.75-6.73 (d, 4H, H_b), 6.69-6.67 (m, 3H, H_g + H_c), 6.53-6.51 (d, 4H, H_a), 4.84 (s, 4H, -NH₂). ¹³C NMR (125 MHz, DMSO-*d*₆, δ, ppm): 145.09 (C⁵), 144.44 (C¹), 143.39 (C⁹), 137.23 (C⁴), 135.04 (C⁸), 129.00 (C¹¹), 125.88 (C³), 120.23 (C⁶), 119.82 (C⁷), 118.04 (C¹²), 114.85 (C¹⁰), 114.81 (C²). Anal. Calcd. (%) for C₂₄H₂₂N₄ (366.46): C, 78.66 %; H, 6.05 %; N, 15.29 %. Found: C, 77.58 %; H, 5.93 %; N, 14.80 %.

N-(4-Methoxyphenyl)-*N'*-(4-nitrophenyl)benzene-1,4-diamine (**1-OMe**)



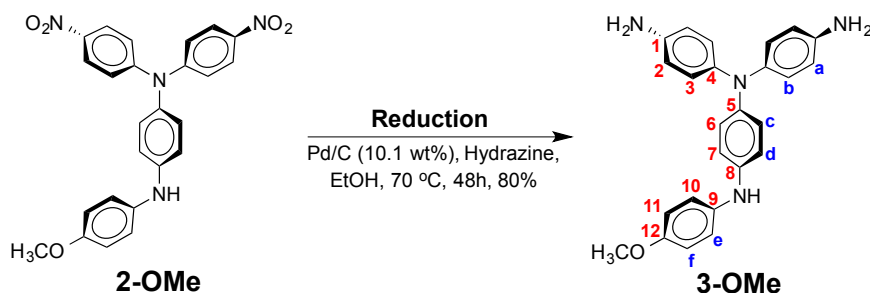
A mixture of 4.28 g (20.0 mmol) of *N*-(4-aminophenyl)-*N*-(4-methoxyphenyl)amine and 2.43 g (24.0 mmol) of triethylamine were added to 40 mL of DMSO at room temperature. 2.96 g (21.0 mmol) of 4-fluoronitrobenzene was then added in sequence. The mixture was heated with stirring at 120 °C for 72 h under nitrogen atmosphere to avoid oxidation of the amine. After the reaction, the mixture was cooled to room temperature and poured into stirred MeOH/H₂O, and the precipitated brown powder was collected by filtration and purified by recrystallization from MeOH. The product was filtered to afford 5.43 g (81% in yield) of deep red powder. m.p.: 178-179 °C measured by DSC at 5 °C/min. IR (KBr): 3360 cm⁻¹ (secondary N-H stretch), 1590 and 1286 cm⁻¹ (-NO₂ stretch). ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm): 8.99 (s, 1H, Ar), 7.99-7.97 (d, 2H, Ar), 7.83 (s, 1H, -NH), 7.04-6.99 (m, 4H, Ar), 6.93-6.91 (d, 2H, Ar), 6.83-6.80 (m, 4H, Ar), 3.67 (s, 3H, -OCH₃). ¹³C NMR (125 MHz, DMSO-*d*₆, δ, ppm): 154.11, 152.77, 142.52, 137.52, 136.67, 130.78, 126.68, 124.40, 120.46, 116.18, 114.94, 112.50, 55.58. Anal. Calcd. (%) for C₁₉H₁₇N₃O₃ (335.36): C, 68.05 %; H, 5.11 %; N, 12.53 %. Found: C, 67.89 %; H, 5.10 %; N, 12.48 %.

N-(4-Methoxyphenyl)-*N'*, *N'*-bis(4-nitrophenyl)benzene-1,4-diamine (2-OMe)



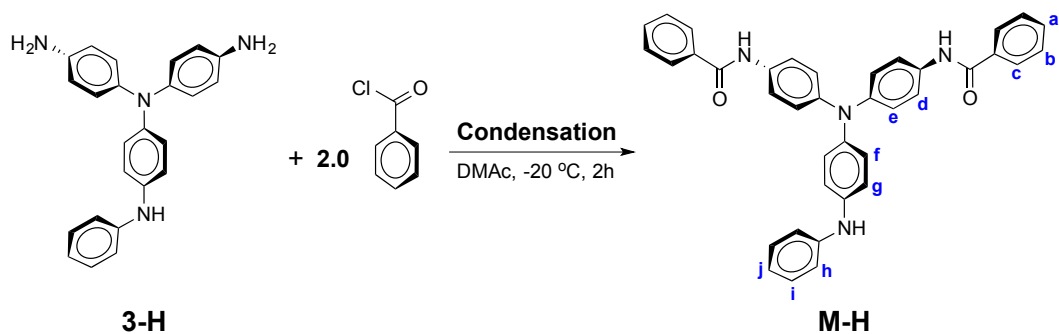
A mixture of 3.20 g (21.0 mmol) of CsF was added to 30 mL of DMSO at room temperature. The mixture 6.72 g (20.0 mmol) of mono-nitro compound **1-OMe** and 2.96 g (21.0 mmol) of 4-fluoronitrobenzene were added in sequence. The mixture was stirred and heated at 150 °C for 24 h under nitrogen atmosphere. After the reaction, the mixture was poured into 300 mL of stirred methanol slowly, and precipitated dark red powder was collected by filtration and washed thoroughly with water. Reprecipitation from DMF/MeOH gives 7.31 g of dinitro compound **2-OMe** as dark red powder with 80% in yield. m.p.: 201-203 °C measured by DSC at 5 °C/min. IR (KBr): 3388 cm⁻¹ (secondary N-H stretch), 1575 and 1307 cm⁻¹ (-NO₂ stretch). ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm): 8.17-8.13 (m, 5H, N-H and H_a), 7.20-7.18 (d, 4H, H_b), 7.10-7.08 (d, 2H, H_c), 7.06-7.05 (d, 2H, H_c), 6.99-6.97 (d, 2H, H_d), 6.90-6.89 (d, 2H, H_f), 3.72 (s, 3H, -OCH₃). ¹³C NMR (125 MHz, DMSO-*d*₆, δ, ppm): 154.44 (C¹²), 151.76 (C⁴), 144.91 (C⁵), 141.46 (C¹), 135.09 (C⁸), 134.01 (C⁹), 128.87 (C⁶), 125.43 (C²), 121.55 (C¹⁰), 121.51 (C³), 115.53 (C⁷), 114.56 (C¹¹), 55.17 (-OCH₃). Anal. Calcd. (%) for C₂₅H₂₀N₄O₅ (456.45): C, 65.78 %; H, 4.42 %; N, 12.27 %. Found: C, 65.50 %; H, 4.36 %; N, 12.18 %.

N,N-Bis(4-aminophenyl)-*N'*-(4-methoxyphenyl)benzene-1,4-diamine (3-OMe)



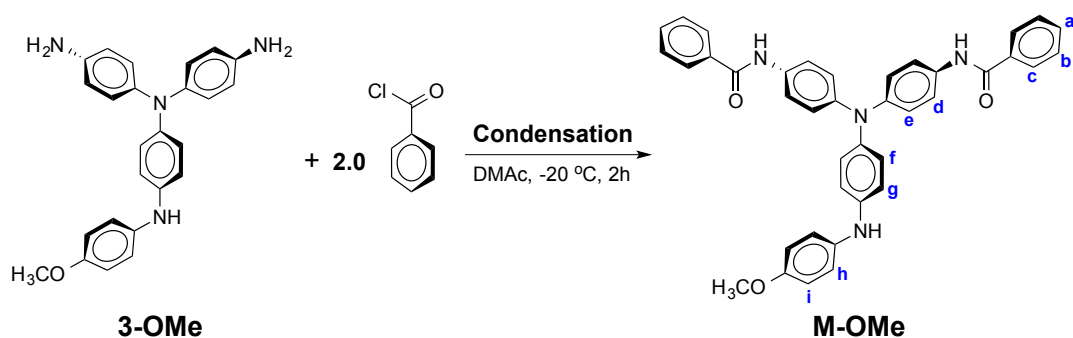
In a 100 mL two-neck round-bottomed flask equipped with a stirring bar under nitrogen atmosphere, 4.56 g (10.0 mmol) of compound **2-OMe** and 0.46 g of 10 % Pd/C were dispersed/suspended in 60 mL of ethanol. The suspension solution was heated to reflux, and 5 mL of hydrazine monohydrate was added slowly to the mixture. After a further 48 h of reflux, the solution was filtered to remove Pd/C, and the filtrate was cooled to precipitate. The product was collected by filtration and dried *in vacuo* at 80 °C to obtain 3.16 g of purple powder (80 % in yield). m.p.: 148-150 °C measured by DSC at 5 °C/min. IR (KBr): 3400-3327 cm⁻¹ (primary and secondary N-H stretch). ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm): 6.93-6.91 (s, 1H, -NH), 6.82-6.80 (d, 2H, H_e), 6.80-6.78 (m, 4H, H_d+H_f), 6.71-6.66 (m, 6H, H_b+H_c), 6.52-6.48 (d, 4H, H_a), 4.79 (s, 4H, -NH₂), 3.67 (s, 3H, -OCH₃). ¹³C NMR (125 MHz, DMSO-*d*₆, δ, ppm): 152.78 (C¹²), 144.04 (C¹), 141.92 (C⁵), 137.83 (C⁸), 137.64 (C⁴), 137.56 (C⁹), 125.31(C³), 121.43 (C⁶), 118.23 (C¹⁰), 117.42 (C⁷), 114.77 (C²), 114.49 (C¹¹), 55.19 (-OCH₃). Anal. Calcd. (%) for C₂₅H₂₄N₄O (396.48): C, 75.73 %; H, 6.10 %; N, 14.13 %. Found: C, 75.04 %; H, 5.98 %; N, 14.00 %.

4,4'-Dibenzoylamide-N,N,N'-triphenylbenzene-1,4-diamine (M-H)



A solution of 0.37 g (1.0 mmol) of **3-H** in 2.0 mL of DMAc was cooled with stirring at -20 °C on an ice/acetone bath. 0.28 g (2.0 mmol) of benzoyl chloride was then added into the mixture. The mixture was then stirred at -20 °C for 2 h and poured into 50 mL of MeOH/H₂O. The precipitated **M-H** was collected by filtration, and dried at 100 °C to obtain 0.38 g (65 % in yield) of light green powder. m.p.: 147-149 °C measured by DSC at 5 °C/min. IR (KBr): 3400-3200 cm⁻¹ (amide and secondary N-H stretch), 1651 cm⁻¹ (amide carbonyl). ¹H NMR (400 MHz, DMSO-*d*₆, δ, ppm): 10.15 (s, 2H, -NHCO-), 8.07 (s, 1H, -NH), 7.91-7.90 (d, 4H, Ar), 7.67-7.63 (d, 4H, Ar), 7.55-7.46 (m, 6H, Ar), 7.19-7.15 (t, 2H, Ar), 7.04-7.00 (t, 4H, Ar), 6.95-6.92 (m, 6H, Ar). 6.76-6.72 (t, 1H, Ar) ¹³C NMR (100 MHz, DMSO-*d*₆, δ, ppm): 165.54, 144.13, 143.99, 140.06, 139.67, 135.41, 133.89, 131.78, 129.53, 128.72, 127.94, 126.26, 123.07, 122.02, 119.66, 118.69, 116.68.

**4,4'-Dibenzoylamide-N,N-diphenylbenzene-N'-(4''-methoxyphenyl)-1,4-diamine
(M-OMe)**

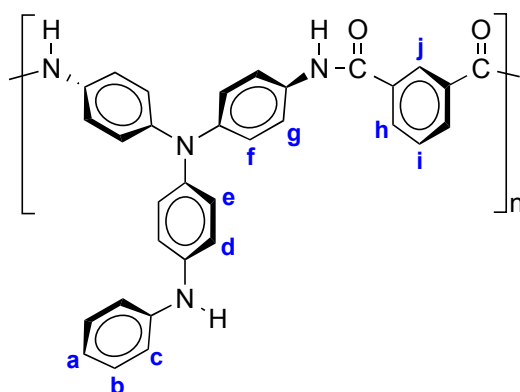


A solution of 0.40 g (1.0 mmol) of **3-OMe** in 2.0 mL of DMAc was cooled with stirring at -20 °C on an ice/acetone bath. 0.28 g (2.0 mmol) of benzoyl chloride was then added into the mixture. The mixture was then stirred at -20 °C for 2 h and poured into 50 mL of stirred H₂O. The precipitated **M-OMe** was collected by filtration, and dried at 100 °C to obtain 0.41 g (68 % in yield) of orange powder. m.p.: 118-120 °C measured by DSC at 5 °C/min. IR (KBr): 3400-3200 cm⁻¹ (amide and secondary N-H stretch), 1654 cm⁻¹ (amide carbonyl). ¹H NMR (400 MHz, DMSO-*d*₆, δ, ppm): 10.16 (s, 2H, amide), 7.95-7.93 (d, 4H, Ar), 7.82 (s, 1H, -NH), 7.72-7.65 (m, 4H, Ar), 7.57-7.49 (m, 6H, Ar), 7.05-6.84 (m, 12H, Ar), 3.70 (s, 3H, -OCH₃). ¹³C NMR (100 MHz, DMSO-*d*₆, δ, ppm): 165.51, 154.03, 144.15, 141.91, 138.65, 136.42, 133.63, 131.76, 128.71, 127.93, 126.92, 122.69, 121.99, 120.44, 116.53, 114.93, 55.59.

Polymer Synthesis

The solution of 0.18 g (0.50 mmol) of diamine **3-H** in 1.0 mL of DMAc was mechanically stirred at room temperature. Liquid nitrogen with ice-bath was used to freeze the solution after the diamine monomer was completely dissolved. And then, 0.10 g (0.50 mmol) of diacid chloride was added in one portion (25 wt% solid content). When the mixture started stirring, 0.10 mL (1.50 mmol) of propylene oxide

was added to the solution. The mixture was mechanically stirred and kept at low temperature (*ca.* -20 °C) for 2 h. The polyamide **PA-H** with inherent viscosity of 1.02 dL/g (measured at a concentration of 0.5 g/dL in H₂SO₄ at 30 °C) could be obtained, showing a high molecular weight of the prepared polyamide. The FT-IR spectrum of polyamide (film) exhibited characteristic amide absorption bands at around 3330 (amide and secondary N-H stretching), and 1655 cm⁻¹ (amide C=O). ¹H NMR (400 MHz, DMSO-*d*₆, δ, ppm): 10.36 (s, 2H, -NH-CO-), 8.51 (s, 1H, -NH), 8.11 (s, 3H, H_h + H_j), 7.71-7.69 (m, 5H, H_g + H_i), 7.20 (s, 2H, H_b), 7.05-6.98 (m, 10H, H_c + H_d + H_e + H_f), 6.77 (s, 1H, H_a). Anal. Calcd. (%) for C₂₅H₂₄N₄O (496.56): C, 77.40 %; H, 4.87 %; N, 11.28 %. Found: C, 72.71 %; H, 5.39 %; N, 11.29 %.



Preparation of the Polyamide Films

Polyamides were prepared by low temperature method using propylene oxide as an acid acceptor. After the clear and viscous polymer solution was obtained, it can directly poured into a 5 cm glass Petri dish, which was then heated in oven at 80 °C for 5 h to remove most of the solvent and byproduct and the semi-dried film was further dried *in vacuo* at 160 °C for 10 h. The obtained films were about 25-35 μm in thickness and were used for solubility tests and thermal analyses.

Measurements

Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 Model FT-IR spectrometer. Elemental analyses were run in a Heraeus

VarioEL-III CHNS elemental analyzer. ^1H NMR spectra were measured on a Bruker AVANCE-500 or 400 FT-NMR using tetramethylsilane as the internal standard, and peak multiplicity was reported as follows: s, singlet; d, doublet. The inherent viscosities were determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at 30 °C. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 6-8 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm³/min) at a heating rate of 20 °C/min. Thermal Mechanical Analyzer (TMA) was conducted with a TA instrument TMA Q400. The TMA experiments were conducted from 40 to 400 °C at a scan rate of 10 °C /min with a film/fiber probe under an applied constant load of 200 mN. Electrochemistry was performed with a CH Instruments 611B electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry (CV) was conducted with the use of a three-electrode cell in which ITO (polymer films area about 0.5 cm x 1.1 cm) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken by using a homemade Ag/AgCl, KCl (sat.) reference electrode. Spectroelectrochemical experiments were carried out in a cell built from a 1 cm commercial UV-visible cuvette using Hewlett-Packard 8453 UV-Visible diode array spectrophotometer. The ITO-coated glass slide was used as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl cell as the reference electrode. The thickness of the polyamide thin films was measured by alpha-step profilometer (Kosaka Lab., Surfcoorder ET3000, Japan).

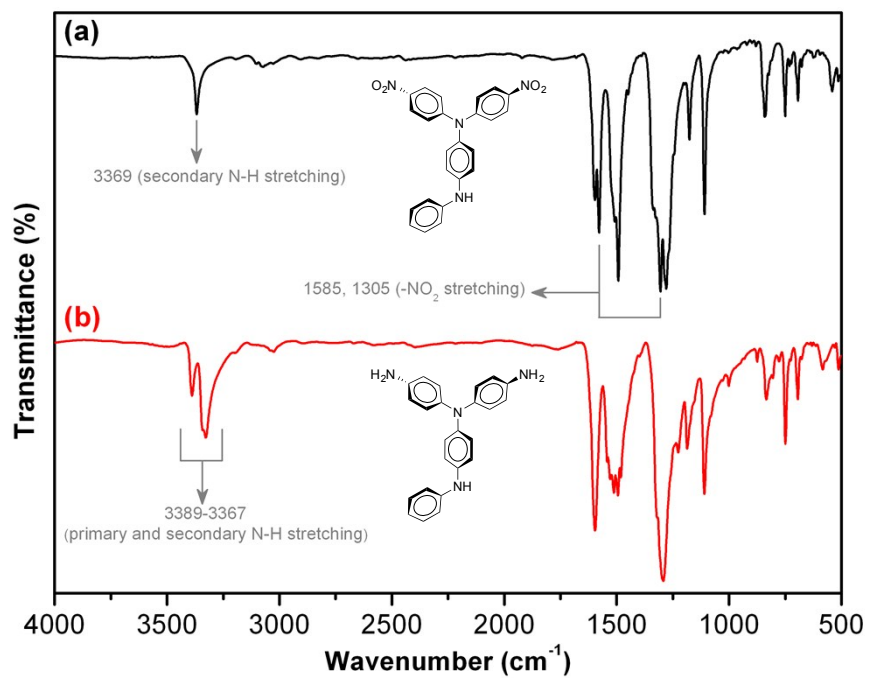


Figure S1. FT-IR spectra of compounds (a) **2-H** and (b) **3-H**.

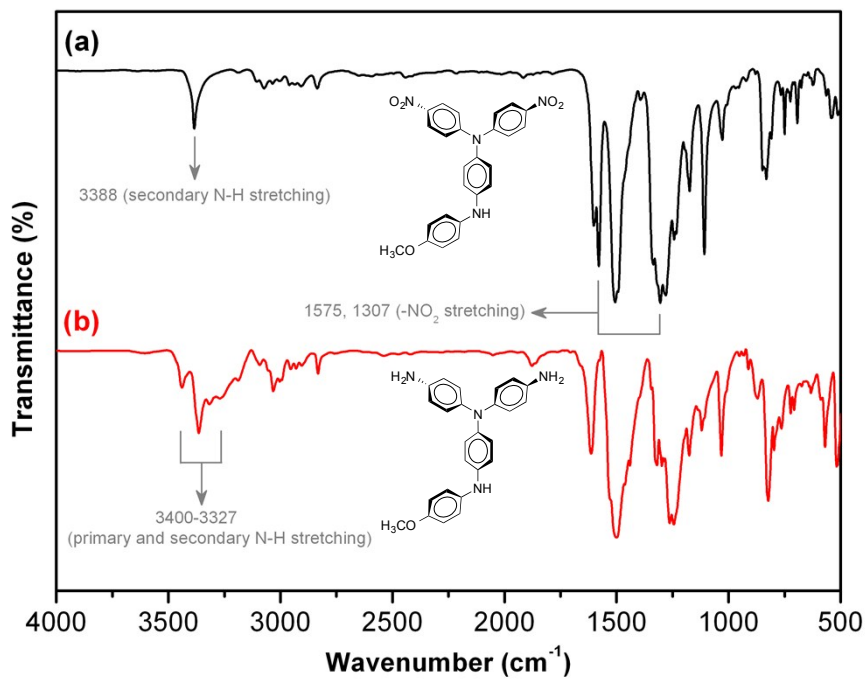


Figure S2. FT-IR spectra of compounds (a) 2-OMe and (b) 3-OMe.

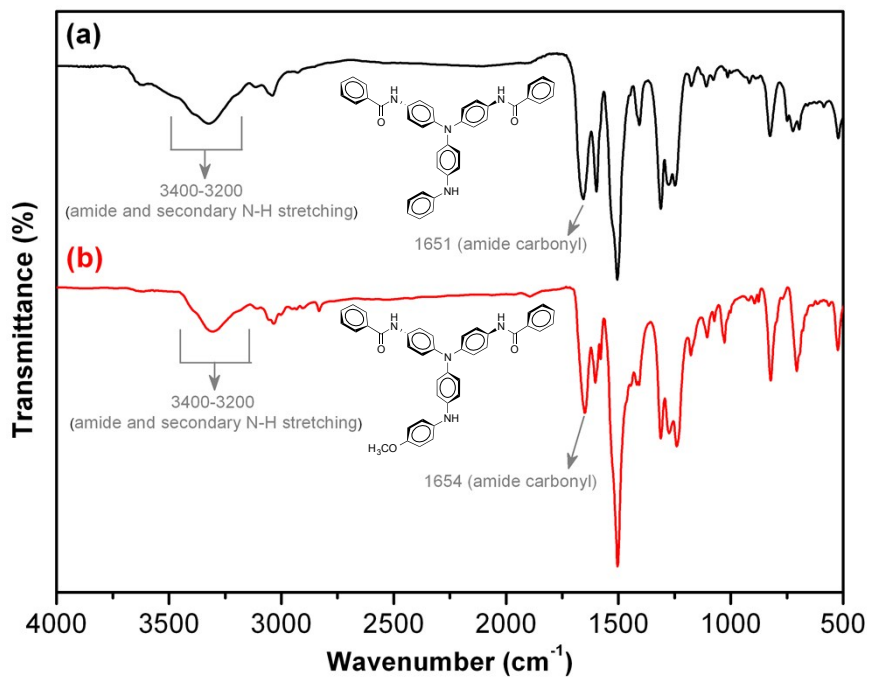


Figure S3. FT-IR spectra of model compounds (a) **M-H** and (b) **M-OMe**.

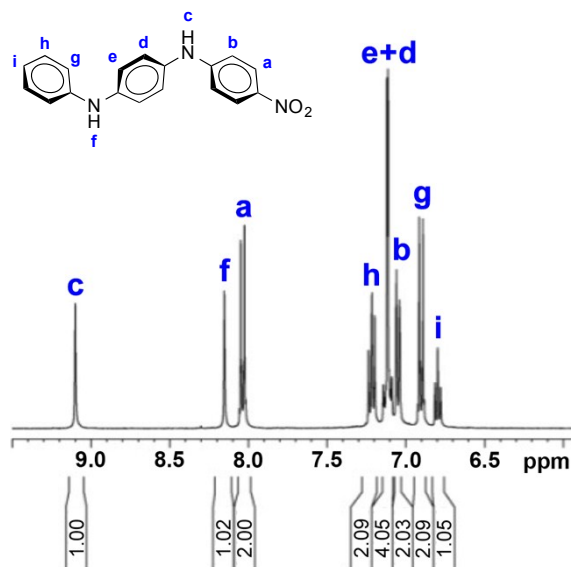


Figure S4. ¹H-NMR spectra of **1-H** in DMSO-*d*₆.

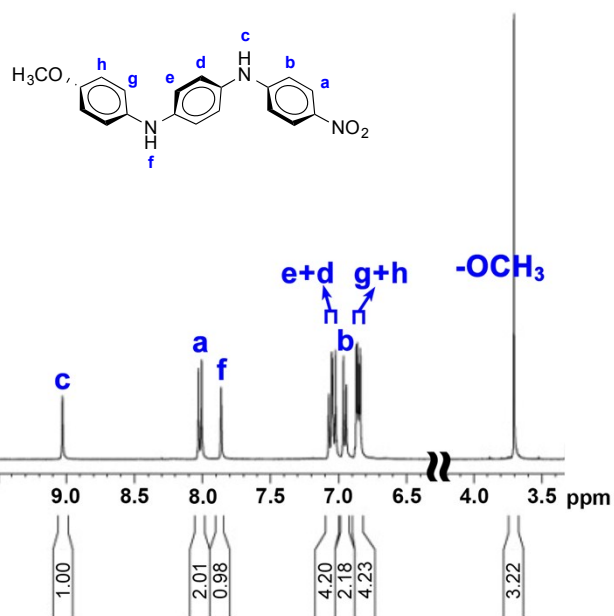


Figure S5. ¹H-NMR spectra of **1-OMe** in DMSO-*d*₆.

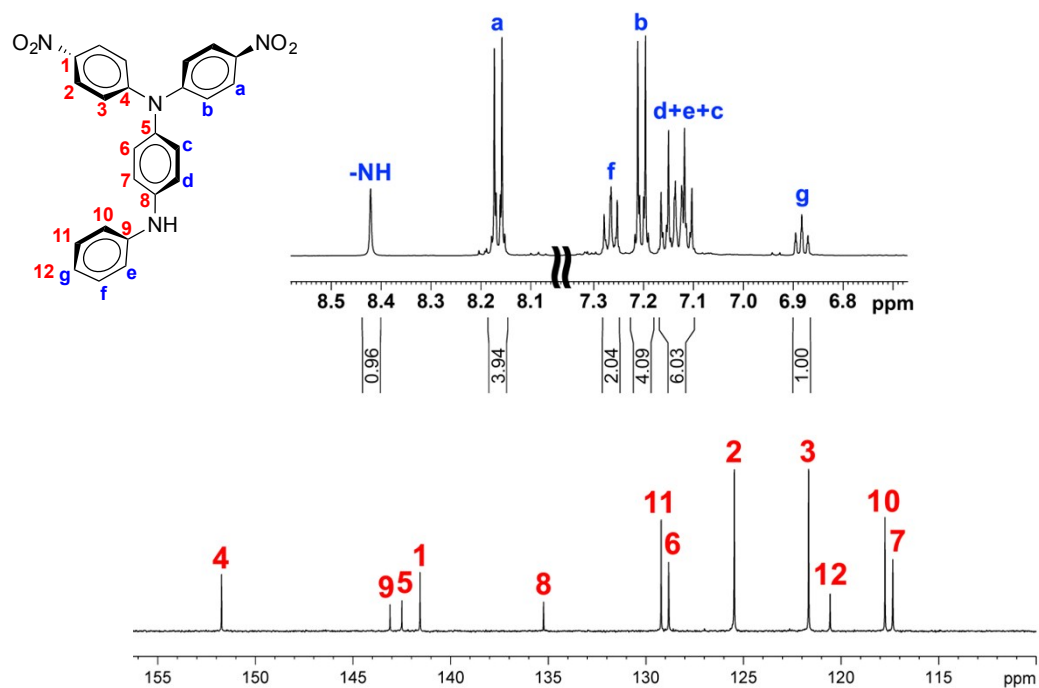


Figure S6. (top) ^1H -NMR spectra and (bottom) ^{13}C -NMR spectra of **2-H** in $\text{DMSO-}d_6$.

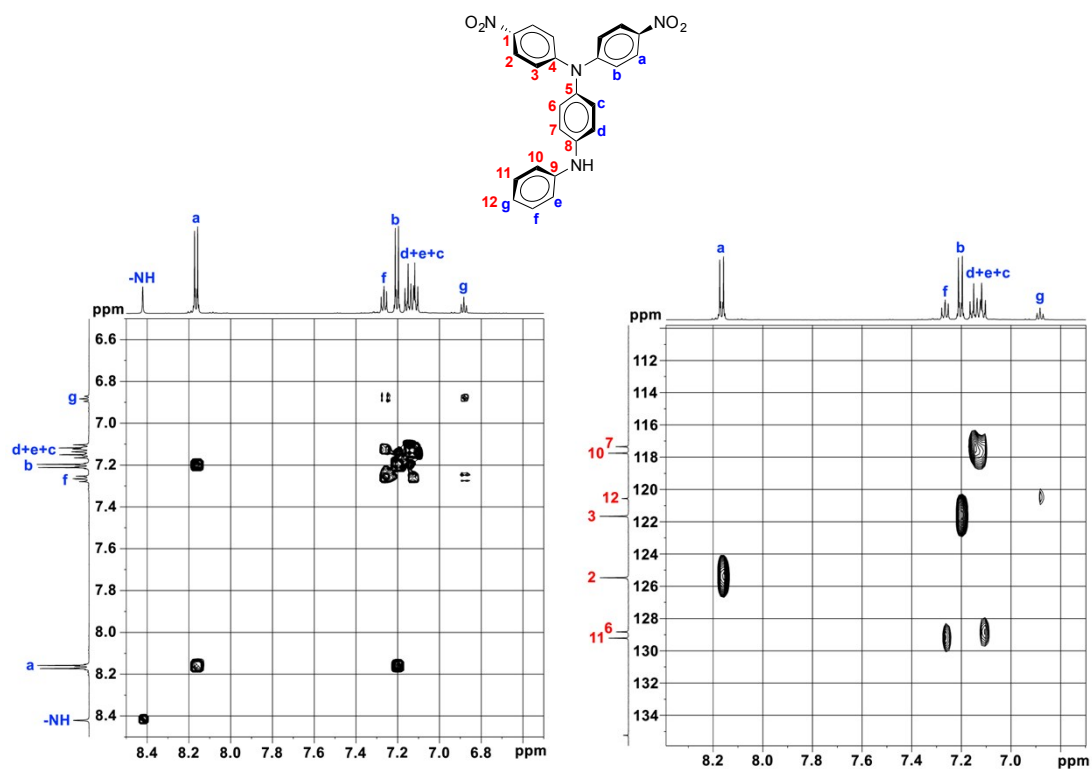


Figure S7. (left) H-H COSY and (right) C-H HSQC spectra of **2-H** in $\text{DMSO-}d_6$.

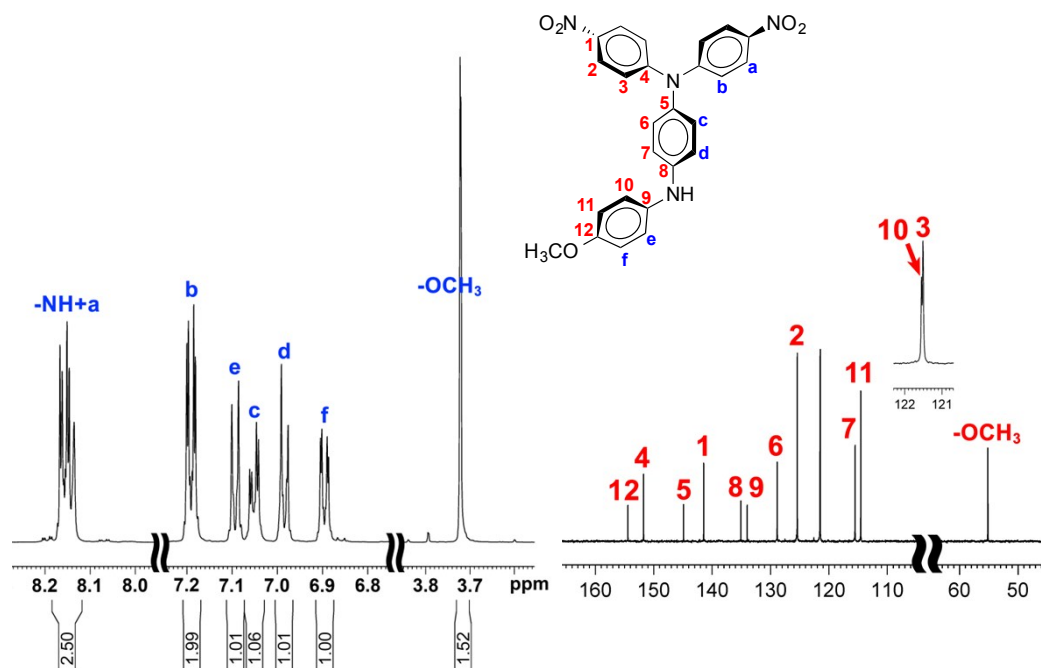


Figure S8. (left) ^1H -NMR spectra and (right) ^{13}C -NMR spectra of **2-OMe** in $\text{DMSO-}d_6$.

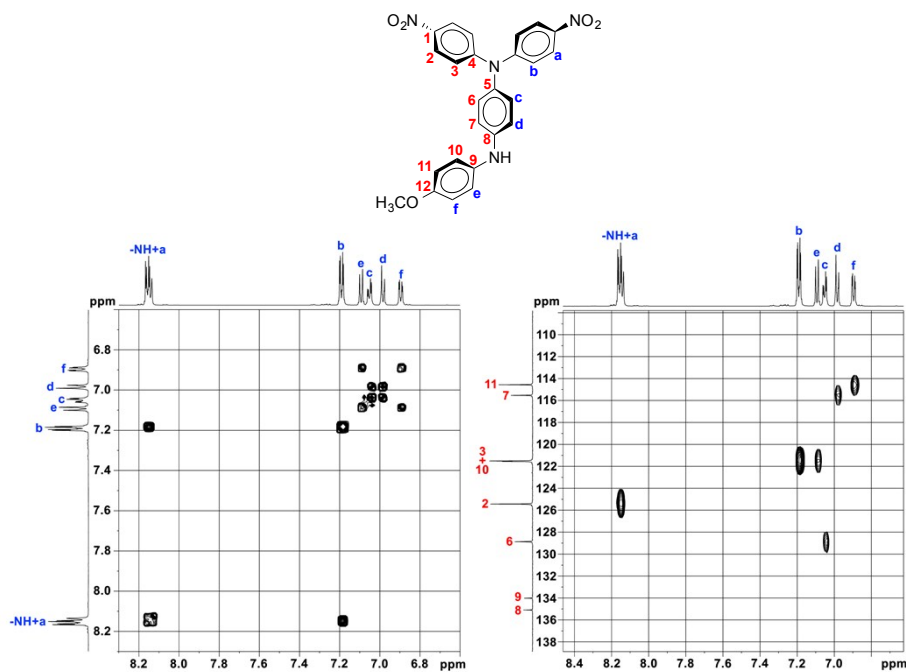


Figure S9. (left) H-H COSY and (right) C-H HSQC spectra of **2-OMe** in $\text{DMSO-}d_6$.

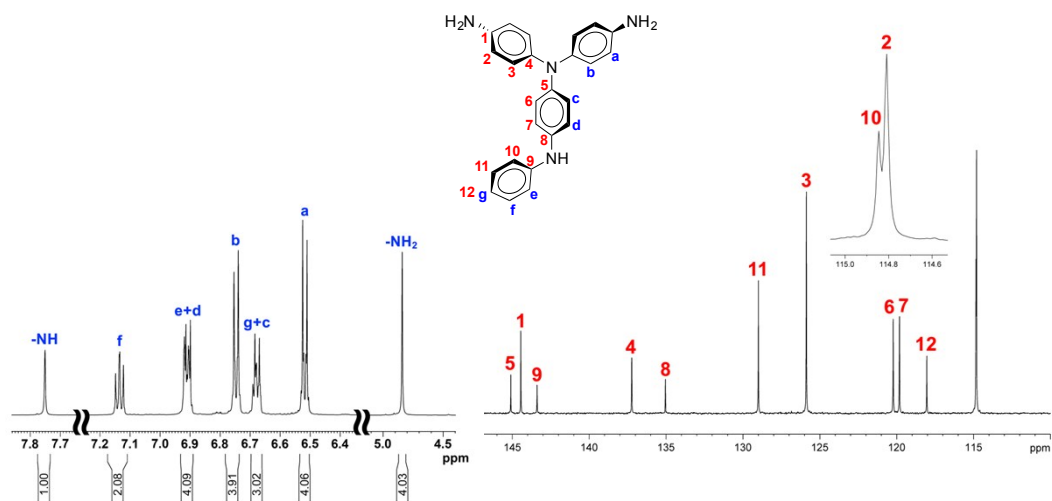


Figure S10. (left) ^1H -NMR spectra and (right) ^{13}C -NMR spectra of **3-H** in $\text{DMSO-}d_6$.

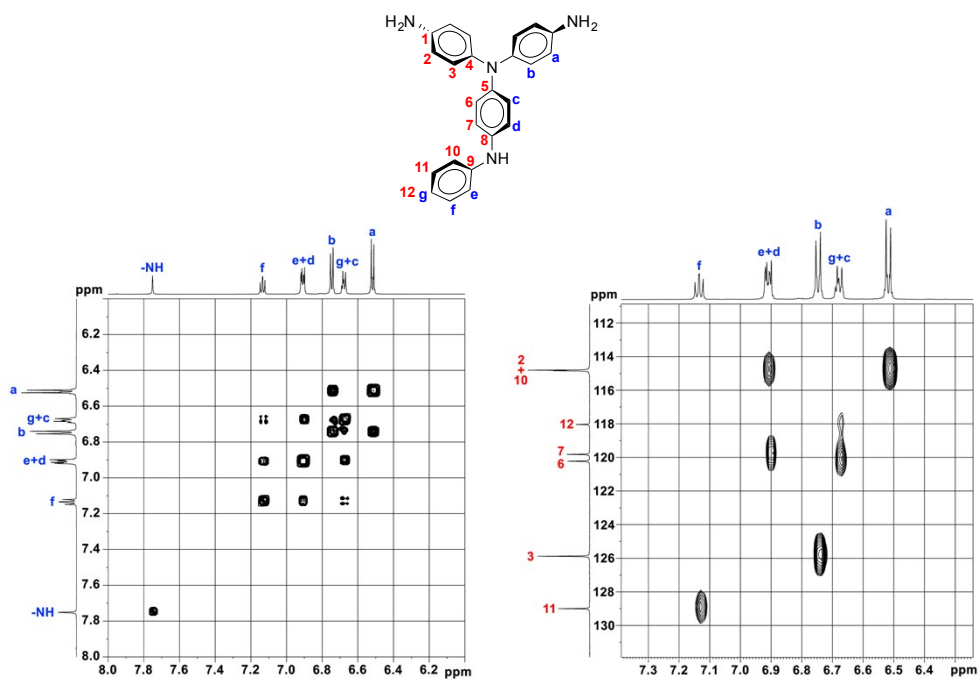


Figure S11. (left) H-H COSY and (right) C-H HSQC spectra of **3-H** in $\text{DMSO-}d_6$.

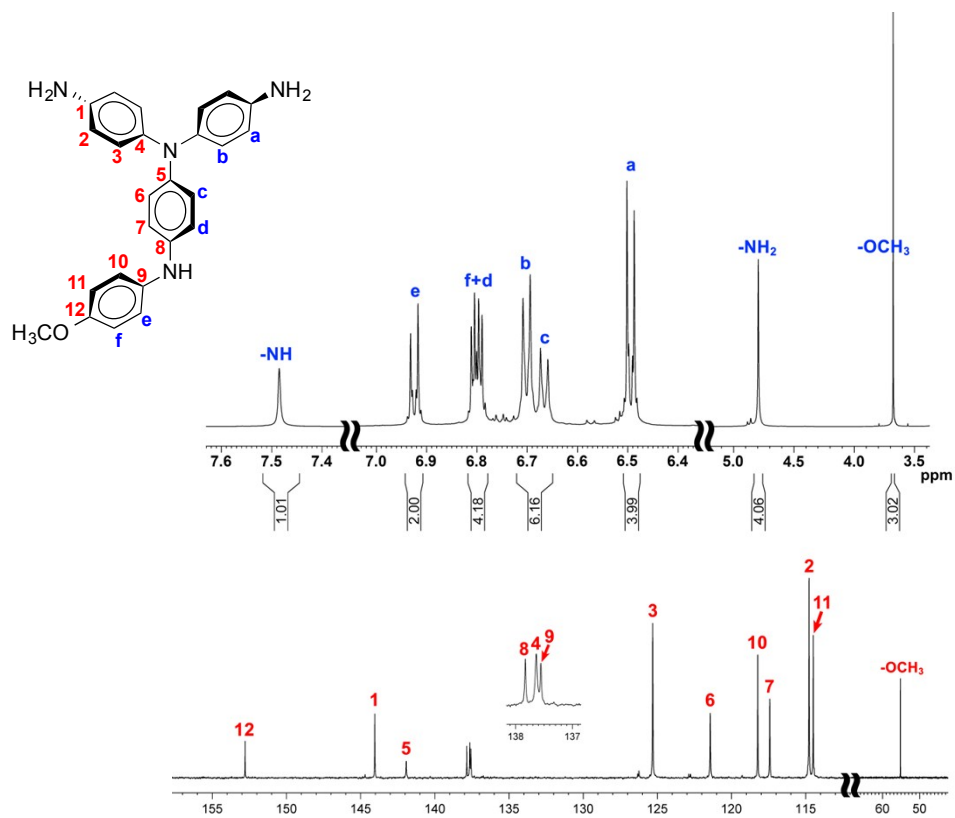


Figure S12. (top) ^1H -NMR spectra and (bottom) ^{13}C -NMR spectra of **3-OMe** in $\text{DMSO-}d_6$.

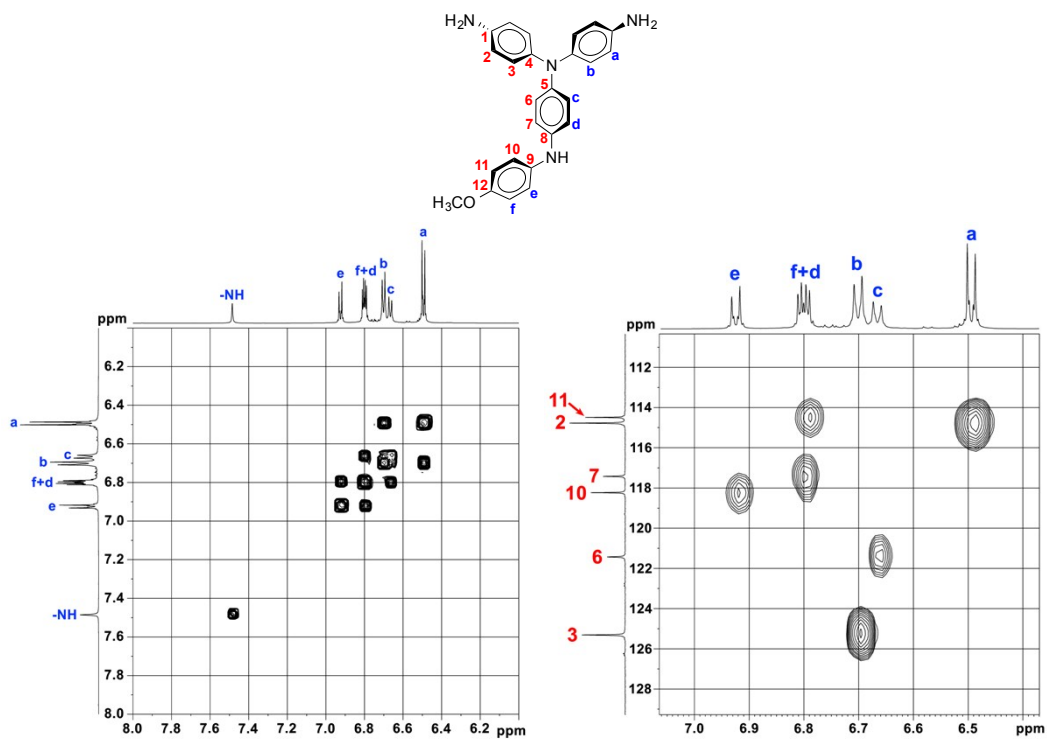


Figure S13. (left) H-H COSY and (right) C-H HSQC spectra of **3-OMe** in $\text{DMSO-}d_6$.

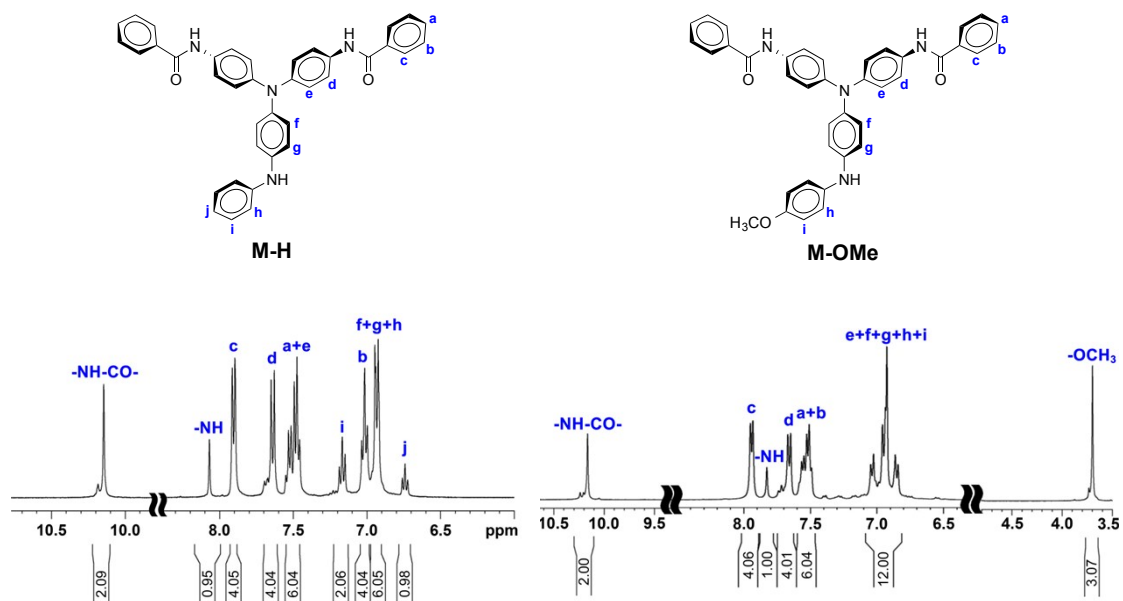


Figure S14. ¹H-NMR spectra of model compounds (left) **M-H** and (right) **M-OMe** in DMSO-*d*₆.

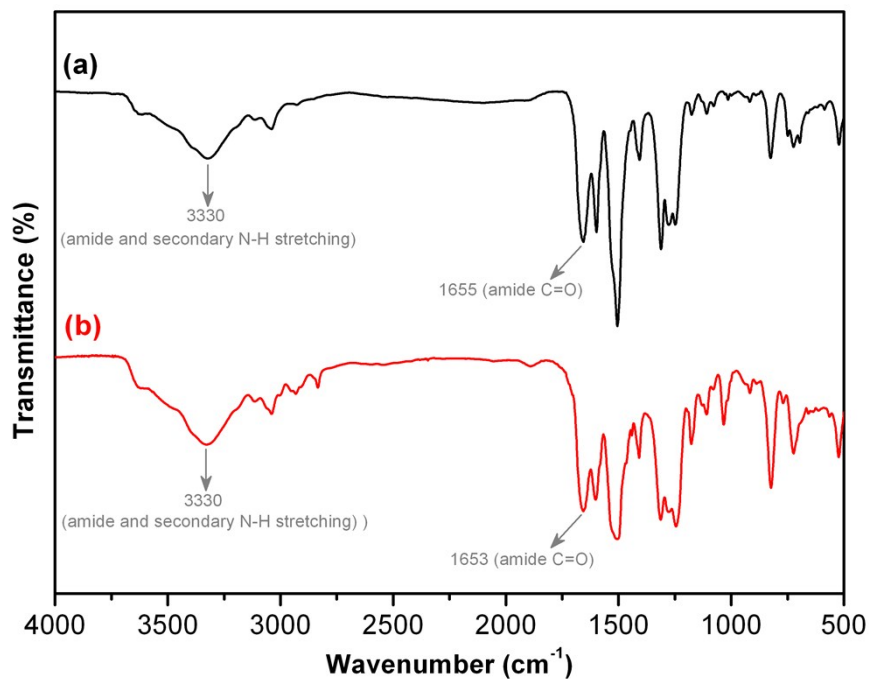


Figure S15. IR spectra of polyamides (a) PA-H (b) PA-OMe.

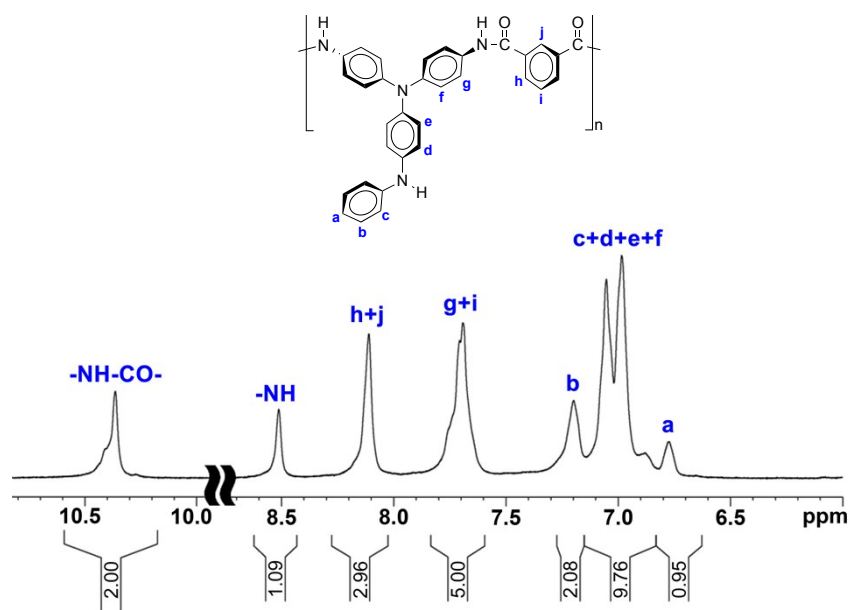


Figure S16. ^1H NMR of polyamide PA-H in $\text{DMSO-}d_6$.

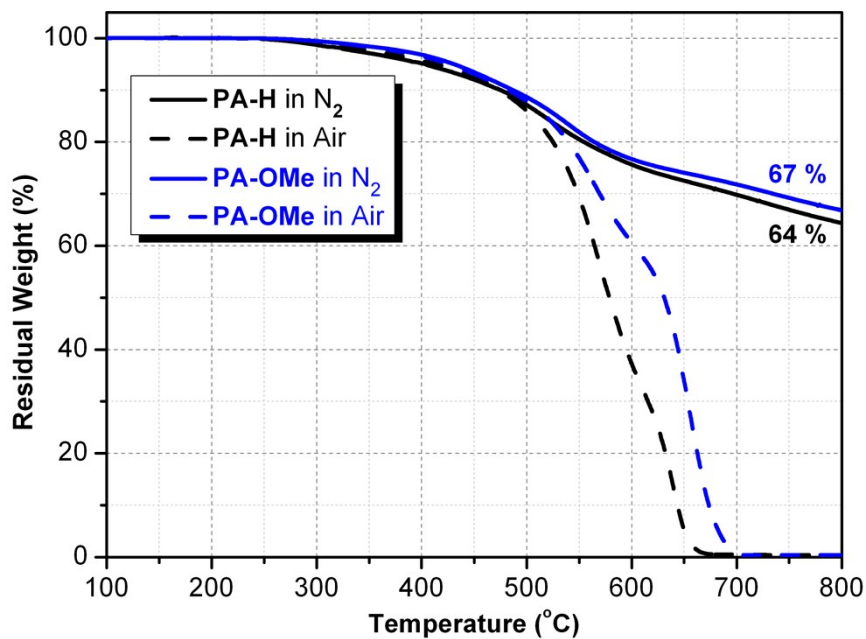


Figure S17. TGA thermograms of polyamides **PA-H** and **PA-OMe** in both air and nitrogen at a scan rate of 20 °C/min.

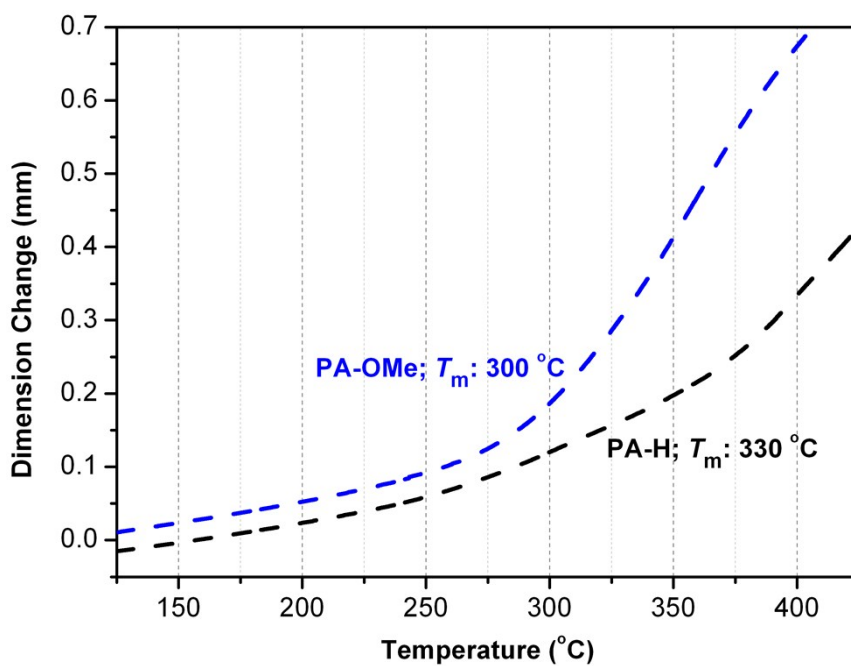


Figure S18. TMA curves of polyamides **PA-H** and **PA-OMe** at a scan rate of 10 °C/min.

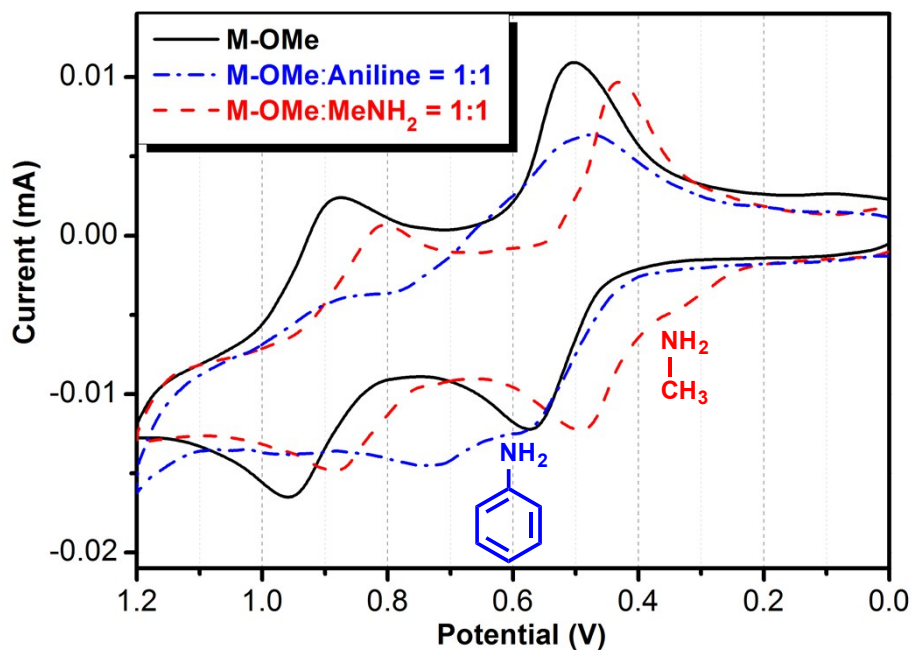


Figure S19. Cyclic voltammograms of M-OMe with equal molar of aniline and methylamine, respectively.

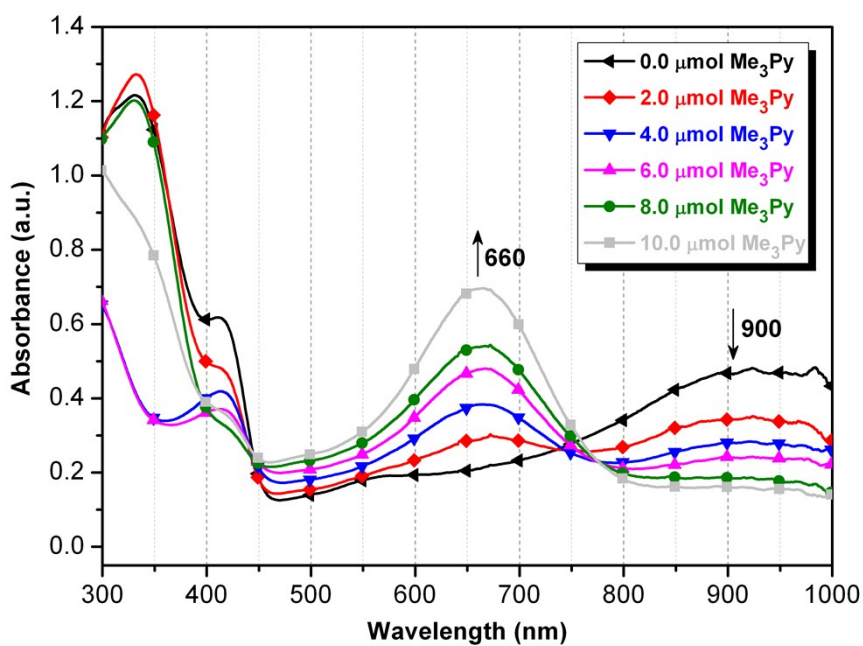


Figure S20. Absorption spectra change of 10 μmol M-OMe in 0.1 M TBAP/CH₃CN with various amount of Me₃Py [$pK_a=7.48$] at 0.45 (V vs. Ag/AgCl).

Table S1. Inherent Viscosity and Solubility Behavior of Polyamides

Code	η_{inh}^a (dL/g)	Solubility in various solvents ^b						
		NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF	CHCl ₃
PA-H	1.02	±	±	±	±	±	—	—
PA-OMe	0.95	±	±	±	±	±	—	—

^a Measured at a polymer concentration of 0.5 g dL⁻¹ in H₂SO₄ at 30 °C.

^b Qualitative solubility was tested with 1 mg of a sample in 1 mL of solvent. ±, partially soluble or swelling; —, insoluble even on heating.

Table S2. Thermal Properties of Polyamides

Polymer ^a	T_s (°C) ^b	T_d^5 (°C) ^c		T_d^{10} (°C) ^c		R_{w800} (%) ^d	LOI ^e
		N ₂	Air	N ₂	Air		
PA-H	330	415	405	475	475	64	43
PA-OMe	300	430	425	485	480	67	44

^a The polymer film samples were heated at 250 °C for 1 h prior to all the thermal analyses.

^b Softening temperature measured by TMA with a constant applied load of 200 mN at a heating rate of 10 °C/min by film/fiber probe in nitrogen.

^c Temperature at which 5 % and 10 % weight loss occurred, respectively, recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 20 cm³/min.

^d Residual weight percentages at 800 °C under nitrogen flow.

^e LOI = Limiting Oxygen Index = (17.5+0.4×char yield)