**Supplementary Information**

**Boosting *m*-aramids performance with *p*-oriented aromatic amide side chains**

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**S1. Synthesis and characterization of the intermediates and monomer**

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| **Figure S1.** Synthesis of monomer **m** and intermediates |

***Synthesis of 5-(4-nitrobenzamido) isophthalic acid*** *(****1****):*

1.23 g (6.9 mmol) of 4-nitrobenzoyl chloride was added to a pressure flask, together with 1.25 g (6.9 mmol) of 5-aminoisophthalic acid and 50 mL of ethyl acetate. The mixture was stirred for 2 hours at 120 °C, cooled at room temperature and the solid thus obtained was filtered. Yield 97 %.

1H NMR (300 MHz, DMSO-*d6*, δ) = δ 12.91 (s, 2H, COOH), 10.87 (s, 1H, NH), 8.65 (s, 2H, Ph), 8.33 (d, *J* = 8.7 Hz, 2H, Ph), 8.23 (s, 1H, Ph), 8.21 (d, *J* = 8.6 Hz, 2H, Ph). 13C NMR (75.5 MHz, DMSO-*d6*, δ) = 166.57, 164.16, 149.37, 139.94, 139.53, 131.79, 129.41, 125.53, 124.91, 123.65. HRMS (ESI) calculated for ([C15H10N2O7]-H)-: 329.04; found: 329.04. FT-IR [wavenumbers (cm-1)]: ʋCOO-H: 2500-3100, ʋC=O: 1736, 1685. ʋNO2:1518, 1335.

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|  | a) |
| b) | c) |
| **Figure S2**. Characterization of **(1)**. a) FTIR, b) 1H NMR, c) 13C NMR. | |

***Synthesis of 5-(4-aminobenzamido) isophthalic acid (2):***

1.83 g (5.54 mmol) of 5-(4-nitrobenzamido)isophthalic acid (**1**), 91 mg of 10 % Pd/C, and 100 mL of DMF were put together in a hydrogenation flask. The mixture was shaken at 50 °C for 30 min, with a hydrogen pressure of 70 psi. Once cooled at room temperature, the mixture was filtered off using a pad of celite, and the solution was precipitated in water. Finally, the solid was filtered and compound (**2**) was obtained. Yield 85 %.

1H NMR (300 MHz, DMSO-*d6*, δ) = δ 13.21 (s, 2H, COOH), 10.14 (s, 1H, NH), 8.66 (d, *J* = 1.4 Hz, 2H, Ph), 8.16 (s, 1H, Ph), 7.77 (d, *J* = 8.5 Hz, 2H, Ph), 6.61 (d, *J* = 8.5 Hz, 2H, Ph), 5.83 (s, 2H, NH2). 13C NMR (75.5 MHz, DMSO-*d6*, δ) = 166.69, 165.54, 152.42, 140.54, 131.49, 129.58, 124.51, 124.26, 120.41, 112.65. HRMS (ESI) calculated for ([C15H12N2O5]-H)-: 299.07; found: 299.07. FT-IR [wavenumbers (cm-1)]: ʋCOO-H: 2500-3100, ʋC=O: 1662.

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|  | a) |
| b) | c) |
| **Figure S3**. Characterization of (**2**). a) FTIR, b) 1H NMR, c) 13C NMR. | |

***Synthesis of 5-(4-(4-nitrobenzamido)benzamido) isophthalic acid (3):***

5.5 g (0.018 mol) of **2** was dissolved in 250 mL of ethyl acetate in a pressure round-bottom flask. 4.08 g (0.022 mol) of 4-nitrobenzoyl chloride was added. And the solution was stirred for 5 hours at 120 °C. Then, the mixture is cooled at room temperature and the solid thus formed was filtered. Yield 91%.

1H NMR (300 MHz, DMSO-*d*6, δ) = 13.27 (s, 2H, COOH), 10.84 (s, 1H, NH), 10.53 (s, 1H, NH), 8.69 (d, *J* = 1.6 Hz, 2H, Ph), 8.39 (d, *J* = 9.0 Hz, 2H, Ph), 8.26 – 8.18 (m, 3H, Ph), 8.07 (d, *J* = 8.9 Hz, 2H, Ph), 7.96 (d, *J* = 9.0 Hz, 2H, Ph). 13C NMR (75.5 MHz, DMSO-d6, δ) = 166.87, 165.13, 164.82, 139.34, 135.12, 132.57, 132.08, 131.06, 130.79, 128.85, 128.69, 128.62, 127.12, 116.23, 112.91. HRMS (ESI) calculated for ([C22H16N2O6]-H)-: 403.10; found 403.09. FT-IR [wavenumbers (cm-1)]: ʋCOO-H: 2500-3500, ʋC=O: 1651. ʋNO2: 1535, 1321.

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|  | a) |
| b) | c) |
| **Figure S4**. Characterization of **(3)**. a) FTIR, b) 1H NMR, c) 13C NMR | |

***Synthesis of 5-(4-(4-aminobenzamido)benzamido isophthalic acid (4)*:**

10 g (0.022 mol) of **3** was dissolved in 25 mL of DMF and 0.25 g of 10% Pd/C was added to the reaction flask. The mixture was shaken at 50 °C for 30 min, with a hydrogen pressure of 70 psi. Then, it was filtered off using a pad of celite, the solvent is partially eliminated using a rotavapor and the solution was precipitated in water. The solid thus formed is filtered and washed with water. Yield 95%.

1H NMR (300 MHz, DMSO-*d*6, δ) = 13.27 (s, 2H, COOH), 10.47 (s, 1H, NH), 10.04 (s, 1H, NH), 8.69 (d, *J* = 1.6 Hz, 2H, Ph), 8.21 (t, *J* = 1.6 Hz, 1H, Ph), 8.01 (d, *J* = 9.0 Hz, 2H, Ph), 7.94 (d, *J* = 6.9 Hz, 2H, Ph), 7.76 (d, *J* = 8.8 Hz, 2H, Ph), 6.62 (d, *J* = 8.7 Hz, 2H, Ph), 5.78 (s, 2H, NH2). 13C NMR (75.5 MHz, DMSO-*d6*, δ) = 166.65, 165.61, 165.31, 162.35, 152.51, 143.32, 140.10, 131.70, 129.64, 128.58, 128.15, 124.83, 124.70, 120.67, 119.15, 112.63. HRMS (ESI) calculated for ([C22H17N3O6]-H)-: 419.11; found: 419.11. FT-IR [wavenumbers (cm-1)]: ʋN-H: 3200-3500, ʋCOO-H: 3000-3200, ʋC=O: 1687.

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|  | a) |
| b) | c) |
| **Figure S5**. Characterization of **(4)**. a) FTIR, b) 1H NMR, c) 13C NMR | |

***Synthesis of 5-(4-(4-(4-nitrobenzamido)benzamido)benzamido) isophthalic acid (5):***

9.55 g (0.022 mol) of **4** was dissolved in 20 mL of DMA in a pressure round-bottom flask. 5.06 g (0.027 mol) of 4-nitrobenzoyl chloride was added, and the solution was stirred at room temperature overnight. Then, the mixture was precipitated in water and the solid thus formed was filtered and washed with water. Yield 87%.

1H NMR (300 MHz, DMSO-*d*6, δ) = 10.83 (s, 1H, NH), 10.51 (s, 1H, NH), 10.46 (s, 1H, NH), 8.69 (d, *J* = 1.5 Hz, 2H, Ph), 8.37 (d, *J* = 8.9 Hz, 2H, Ph), 8.24 – 8.17 (m, 3H, Ph), 8.04 (d, *J* = 8.8 Hz, 4H), 7.97 (d, *J* = 2.4 Hz, 2H, Ph), 7.94 (d, *J* = 2.3 Hz, 2H). 13C NMR (75.5 MHz, DMSO-*d6*, δ) = 166.84, 166.03, 165.33, 164.26, 150.00, 149.34, 142.79, 142.10, 140.26, 140.14, 136.80, 131.81, 130.75, 129.85, 129.42, 128.97, 128.84, 128.76, 125.07, 124.87, 123.70, 123.61, 119.85, 119.61. HRMS (ESI) calculated for ([C29H20N4O9]-H)-: 568,12; found: 568,12. FT-IR [wavenumbers (cm-1)]: ʋCOO-H: 3000-3500, ʋC=O: 1645. ʋNO2:1526, 1321.

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|  | a) |
| b) | c) |
| **Figure S6**. Characterization of **(5)**. a) FTIR, b) 1H NMR, c) 13C NMR | |

***Synthesis of 5-(4-(4-(4-aminobenzamido)benzamido)benzamido) isophthalic acid (6):***

10.6 g (0.019 mol) of **5** was dissolved in 60 mL of DMF and 0.26 g of 10% Pd/C was added to the reaction flask. The mixture was shaken at 50 °C for 30 min, with a hydrogen pressure of 70 psi. Then, it was filtered using a pad of celite, the solvent is partially eliminated using a rotavapor and the solution was precipitated in water. The solid thus formed is filtered and washed with water. Yield 93%.

1H NMR (300 MHz, DMSO-*d6*, δ) = 13.31 (s, 2H), 10.50 (s, 1H), 10.40 (s, 1H), 10.04 (s, 1H), 8.69 (d, J = 1.6 Hz, 2H), 8.21 (t, J = 1.6 Hz, 1H), 8.15 – 7.87 (m, 9H), 7.76 (d, J = 8.7 Hz, 1H), 6.62 (d, J = 8.7 Hz, 2H), 5.83 (s, 2H). 13C NMR (75.5 MHz, DMSO-*d6*, δ) = 166.77, 165.64, 165.39, 165.27, 152.51, 143.29, 142.79, 140.02, 131.91, 129.65, 128.81, 128.67, 128.63, 128.44, 124.93, 124.69, 120.69, 119.45, 119.17, 112.65. HRMS (ESI) calculated for ([C29H22N4O7]-H)-: 538,15; found: 538,15. FT-IR [wavenumbers (cm-1)]: ʋN-H: 3200-3500, ʋCOO-H: 3000-3200, ʋC=O: 1645.

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|  | a) |
| b) | c) |
| **Figure S7**. Characterization of **(6)**. a) FTIR, b) 1H NMR, c) 13C NMR | |

***Synthesis of monomer 5-(4-(4-(4-(4-nitrobenzamido)benzamido)benzamido)benzamido) isophthalic acid (m):***

17.9 g (0.034 mol) of **6** was dissolved in 130 mL of DMA in a pressure round-bottom flask. 6.85 g (0.037 mol) of 4-nitrobenzoyl chloride was added, and the solution was stirred at room temperature overnight. Then, the mixture precipitated in water and the solid thus formed was filtered and washed with water. Yield 84%.

1H NMR (300 MHz, DMSO-*d6*, δ) = 10.82 (s, 1H), 10.57 – 10.33 (m, 3H), 8.70 (d, J = 1.6 Hz, 2H), 8.36 (d, J = 8.8 Hz, 2H), 8.27 – 8.16 (m, 3H), 8.12 – 7.83 (m, 12H). 13C NMR (75.5 MHz, DMSO-*d6*, δ) = 166.72, 165.34, 165.31, 165.26, 164.23, 149.31, 142.80, 142.70, 142.05, 140.23, 140.12, 131.70, 129.81, 129.39, 129.18, 128.80, 128.77, 128.73, 124.96, 124.81, 123.59, 119.79, 119.53. HRMS (ESI) calculated for ([C36H25N5O10]-H)-: 687.16; found: 687.16. FT-IR [wavenumbers (cm-1)]: ʋCOO-H: 3000-3500, ʋC=O: 1648. ʋNO2:1513, 1347.

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|  | a) |
| a) | b) |
| **Figure S8**. Characterization of **(m)**. a) FTIR, b) 1H NMR, c) 13C NMR | |

**S2. Structural characterization of the polymers**

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|  | a) |
| b) | c) |
| **Figure S9**. Characterization of **P1**. a) FTIR, b) 1H NMR, c) 13C NMR | |

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|  | a) |
| b) | c) |
| **Figure S10**. Characterization of **P10**. a) FTIR, b) 1H NMR, c) 13C NMR | |

|  |  |
| --- | --- |
|  | a) |
| b) | c) |
| **Figure S11**. Characterization of **P20**. a) FTIR, b) 1H NMR, c) 13C NMR | |

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| --- | --- |
|  | a) |
| b) | c) |
| **Figure S12**. Characterization of **P50**. a) FTIR, b) 1H NMR, c) 13C NMR | |

**S3. Mechanical performance of the films**

**Table 1.** Mechanical properties of **P1**, **P10**, **P20**, **P50** and reference **MPIA** films

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| **Polymer** | **Young's Modulus (GPa)** | **Tensile Strength (MPa)** | **Elongation at break (%)** |
| **P1** | 2108 ± 35 | 53 ± 13 | 3.5 ± 1.3 |
| **P10** | 2068 ± 12 | 76 ± 9 | 6.3 ± 0.7 |
| **P20** | 2072 ± 54 | 87 ± 15 | 4.3 ± 0.1 |
| **MPIA** a | 1422 ± 216 | 81 ± 13 | 8.5 ± 0.9 |

a Poly(*m*-phenylene isophthalamide) synthesized at the laboratory

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| **Figure S13**. Tensile tests of **P1**, **P10**, **P20** and reference **MPIA** |