

Supporting Information

Organometallic Polymers Based on Fluorene-Bridged Bis-benzimidazolylidene via Direct Ligand-Metal Coordination: Synthesis, Characterization and Optical Properties

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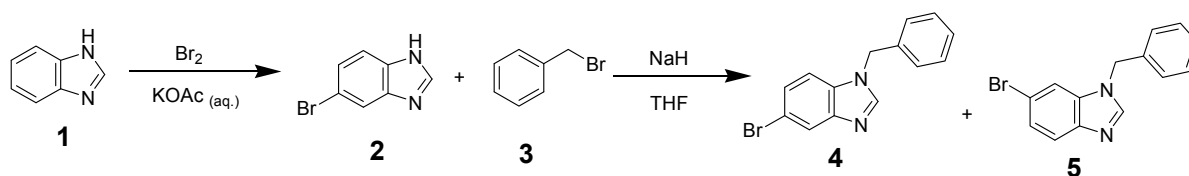
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Synthesis of 5-bromobenzimidazole (2). To a 250-ml two-necked glass reactor was added benzimidazole (**1**: 1.2 g, 10 mmol) and 0.4 M aqueous solution of potassium acetate (100 ml). After cooling in an ice bath, the mixture was dropwise added bromine [0.54 ml (10 mmol) in 120 ml H₂O] under stirring within 30 min, followed by reacting for one day at ambient temperature. The mixture was extracted with dichloromethane three times; the combined organic phase was washed with saturated aqueous solution of sodium chloride and dehydrated with magnesium sulfate anhydrous. The residue obtained after the removal of dichloromethane was further purified by column chromatography using the mixture of ethyl acetate and acetone as an eluent (ethyl acetate/acetone = 3/1). Finally, it was crystallized from ethanol and water to provide as white solid of **2** (Yield: 38%, mp: 131°C). IR (KBr, pellet): ν 3400~2300, 1619, 1043, 869, 808 cm⁻¹; ¹H NMR (DMSO-d₆, ppm): δ 12.61 (s, 1H, -NH), 8.24 (s, 1H, Ar-H), 7.55~7.53 (d, 8.48 Hz, 1H, Ar-H), 7.32~7.30 (dd, 8.48, 1.48 Hz, 1H, Ar-H). Anal. Calcd. for C₇H₅BrN₂: C, 42.67%; H, 2.56%; N, 14.22%. Found: C, 42.55%; H, 2.60%; N, 14.24%.



Scheme S1. Synthetic procedures of monomer **2**, **4** and **5**.

Synthesis of N-benzyl-5-bromobenzimidazole (4) and N-benzyl-6-bromobenzimidazole (5). To a 50-ml glass reactor was added 5-bromobenzimidazole (**2**: 1.40 g, 7.1 mmol) and tetrahydrofuran (THF: 35 ml). The mixture was added with NaH (60% in mineral oil: 0.47 g, 11.7 mmol) under nitrogen purging and then stirred for 30 min. It was added with benzyl bromide (**3**: 1.34 g, 6.4 mmol), refluxed for 6 h, poured into 100 ml de-ionized water, and then extracted with chloroform three times. The combined organic phase was dried with magnesium sulfate anhydrous, followed by the removal of chloroform to obtain mixture of **4** and **5** (50/50). The mixture was separated by column chromatography using ethyl acetate as an eluent, followed with crystallization from ethyl acetate and *n*-hexane to give rise to white solid of **4** (42%) and **5** (33%). Compound **4**: mp = 103~104°C. IR (KBr pellet, cm⁻¹): ν 3070, 3033, 1610, 1045, 900, 871, 730, 700. ¹H NMR (DMSO-d₆, ppm): δ 8.44 (s, 1H, Ar-H), 7.85 (d, 1.20 Hz, 1H, Ar-H), 7.50~7.48 (d, 6.88 Hz, 1H, Ar-H), 7.36~7.27 (m, 6H, Ar-H), 5.50 (s, 2H, -CH₂-). Anal. Calcd. for C₁₄H₁₁BrN₂: C, 58.56%; H, 3.86%; N, 9.76%. Found: C, 58.52%; H, 3.85%; N, 9.75%. Compound **5**: mp = 153~155°C. IR (KBr pellet, cm⁻¹): ν 3085, 3031, 1608, 1045, 890, 852, 738, 696. ¹H-NMR (DMSO-d₆, ppm): δ 8.44 (s, 1H, Ar-H), 7.80 (d, 1.28 Hz, 1H, Ar-H), 7.62~7.60 (d, 6.84 Hz, 1H, Ar-H), 7.36~7.27 (m, 6H, Ar-H), 5.50 (s, 2H, -CH₂-). Anal. Calcd. for C₁₄H₁₁BrN₂: C, 58.56%; H, 3.86%; N, 9.76%. Found: C, 58.52%; H, 3.80%; N, 9.81%.

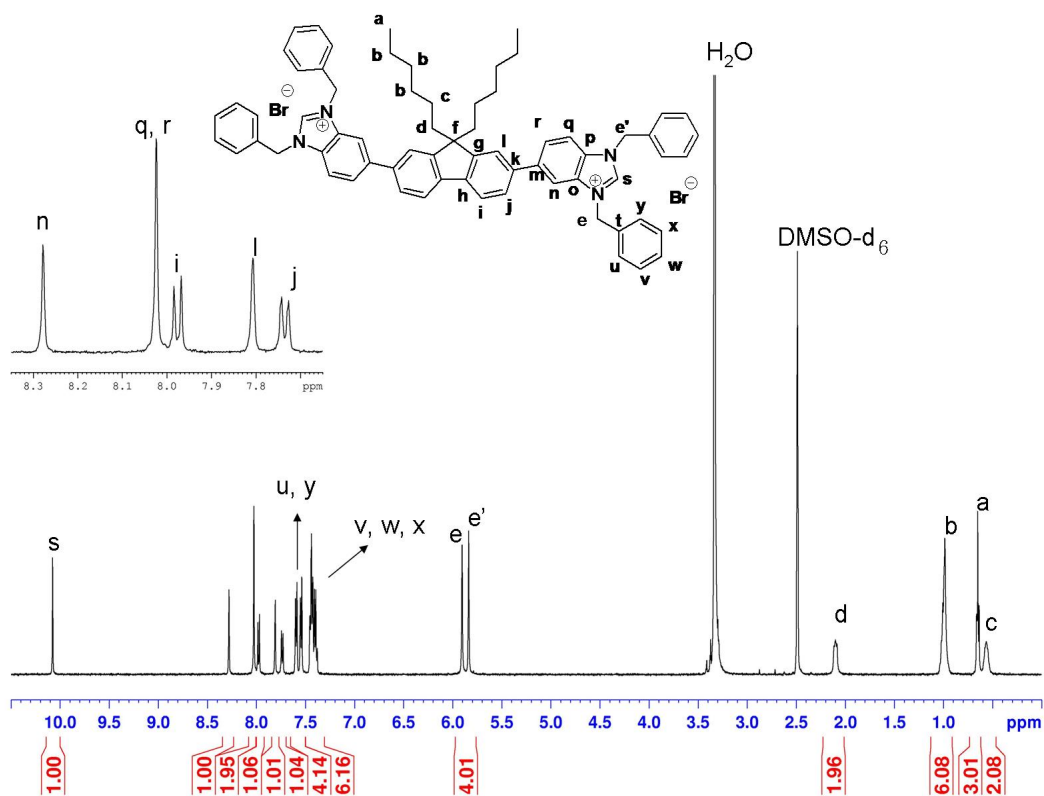


Figure S1. The ^1H -NMR spectrum of monomer **BNM** in DMSO-d_6 .

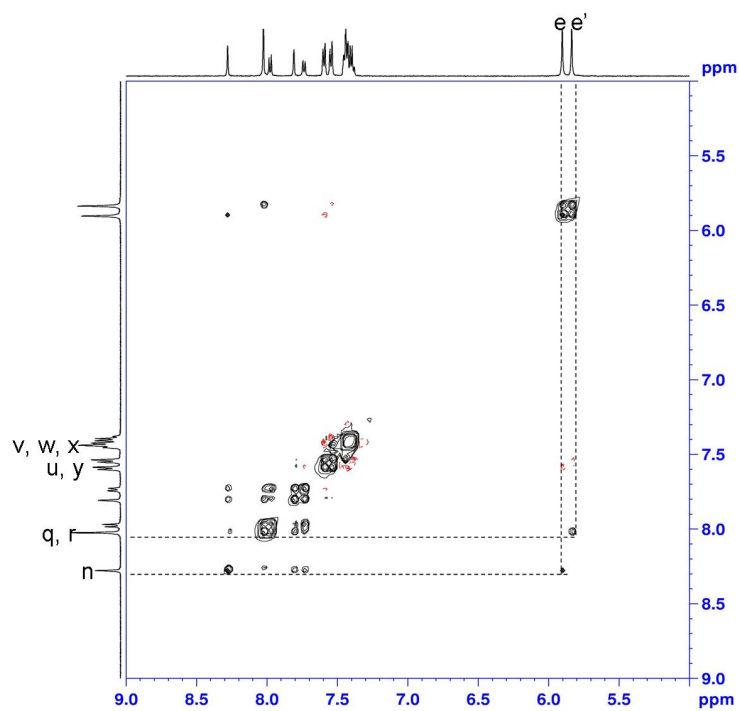


Figure S2. The H-H NOESY spectrum of monomer **BNM** in DMSO-d_6 .

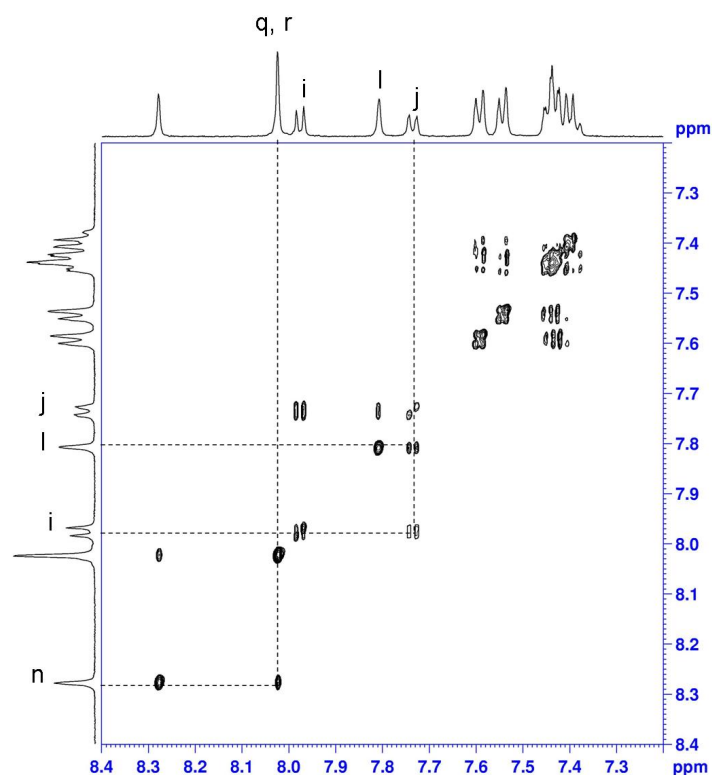


Figure S3. The H-H COSY spectrum of monomer **BNM** in DMSO- d_6 .

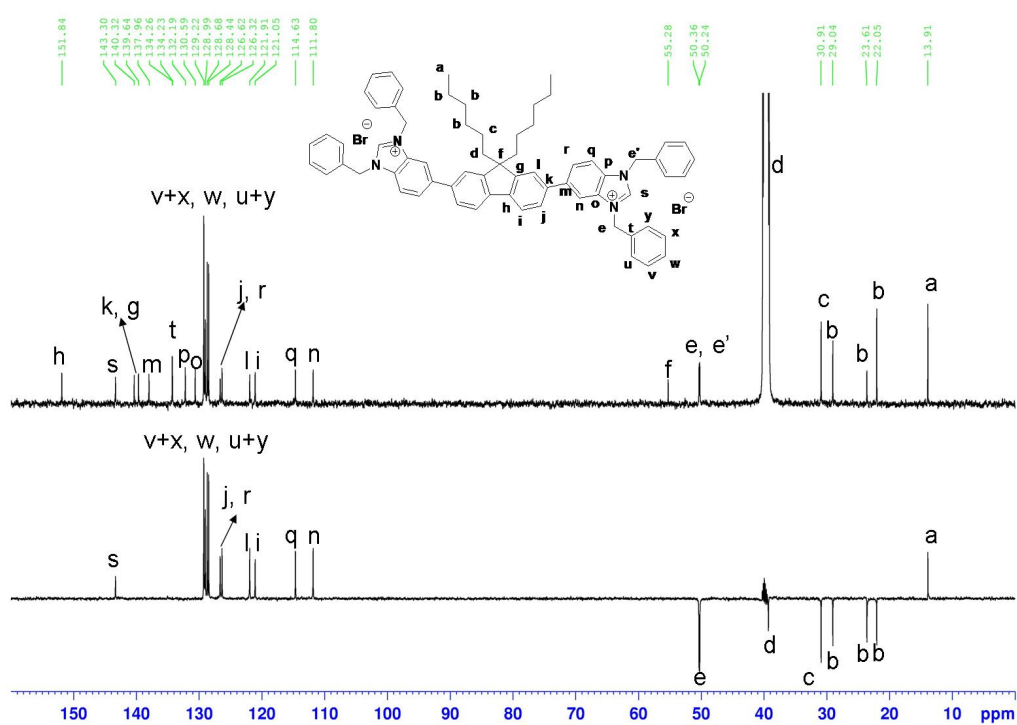


Figure S4. (a) The ^{13}C -NMR spectrum and (b) the DEPT135 spectrum of **BNM** in DMSO- d_6 .

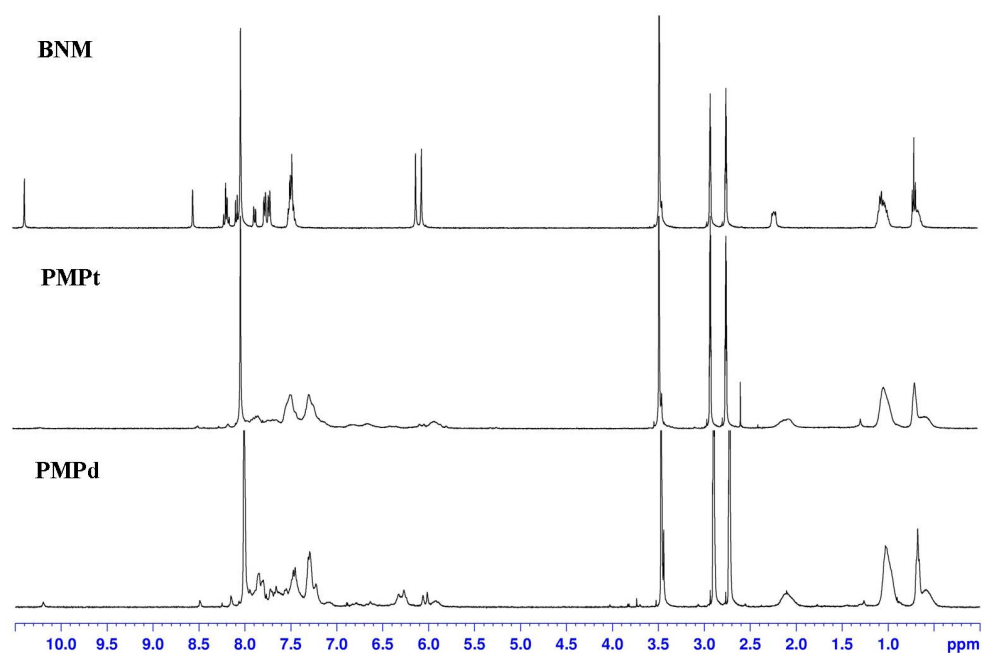


Figure S5. The ^1H -NMR spectra of monomer **BNM**, copolymers **PMPt** and **PMPd** in DMF- d_7 .

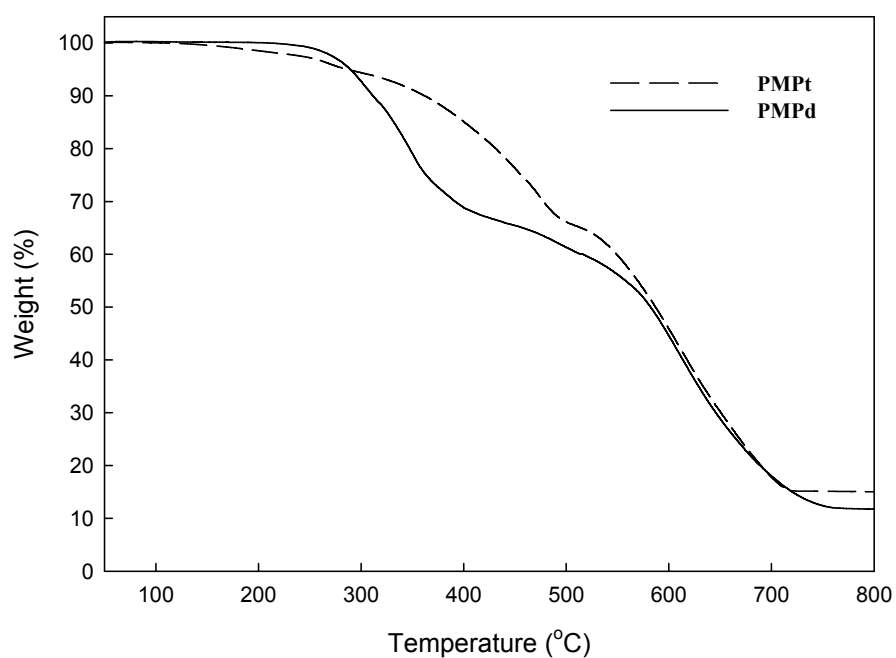


Figure S6. Thermogravimetric curves of **PMPt** and **PMPd** with heating rate of $20^\circ\text{C}/\text{min}$ under nitrogen.

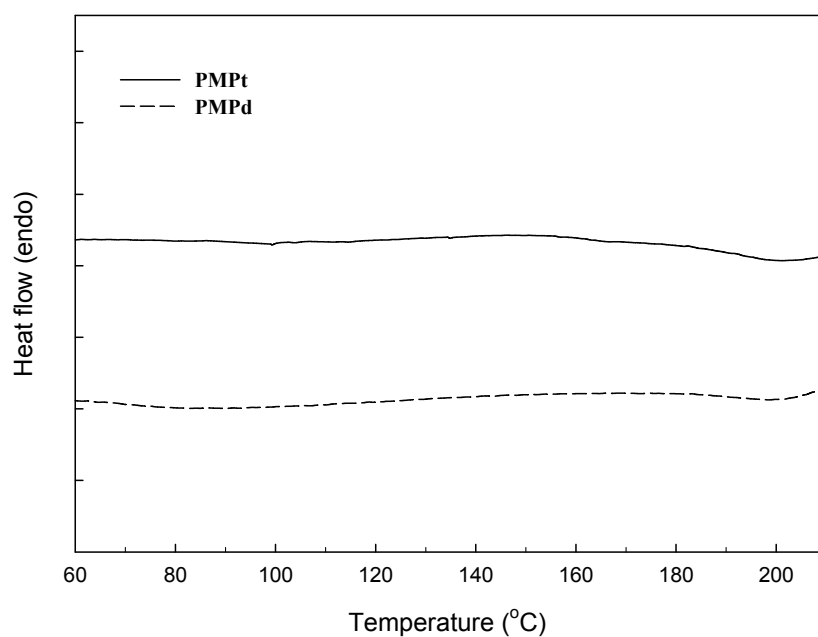


Figure S7. Differential scanning calorimetric curves of **PMPt** and **PMPd** from the second scan with a rate of 20°C/min under nitrogen.