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New π-Conjugated Polymers Containing 1,3,5-Triazine Units in the Main Chain: Synthesis and Optical and Electrochemical Properties of the Polymers

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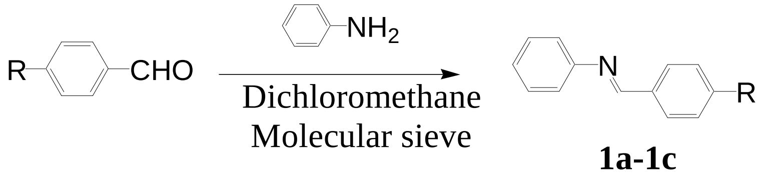
1. Experimental Section

1.1 Materials

9,9-Dioctylfluorene-2,7-bis(trimethyleneborate) was purchased from Aldrich and used as received.

1.2 Synthesis

1.2.1 Preparation of Shiff-bases, **1a-1c**.



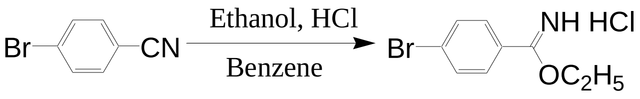
1a-1c

1a, R = H
1b, R = -OCH_3
1c, R = -$N(CH_3)_2$

A mixture of equal molar R-substituted benzaldehyde and aniline, activated 4Å molecular sieve and dichloromethane was stirred at room temperature for overnight under argon atmosphere. After filtration and removing the solvent, the resulting residue was purified by recrystallization from ethanol to give **1a-1c** in yields of 70-80%. ^{1}H-NMR($CDCl_3$), **1a**, δ 8.46 (1H, s), 7.90 (2H, m), 7.48 (3H, m), 7.40 (2H, m), 7.22 (3H, m); **1b**, δ 8.39 (1H, s), 7.85

(2H, d), 7.39 (2H, t), 7.21 (3H, m), 6.98 (2H, d), 3.88 (3H, s); **1c**, δ 8.32 (1H, s), 7.77 (2H, d), 7.36 (2H, t), 7.19 (3H, m), 6.74 (2H, d), 3.06 (6H, s).

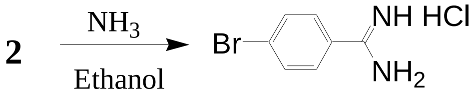
1.2.2 Synthesis of 4-bromobenzimidoethyl ether hydrochloride, **2**.



2

A solution of 100 mmol of 4-bromobenzonitrile and 105 mmol of ethanol in 75 mL of benzene was bubbled by dry HCl for 60 min. After stirring for an additional 5 h at room temperature, the solution was added dropwise to a large of diethyl ether (1 L) to obtain a precipitate, which was filtered and dried *in vacuo* to give **2** in a yield of 83%. ^{1}H NMR ($CDCl_3$), δ 12.68 (1H, m), 11.94 (1H, m), 8.26 (2H, d), 7.72 (2H, d),4.84 (2H, m), 1.65 (3H, t).

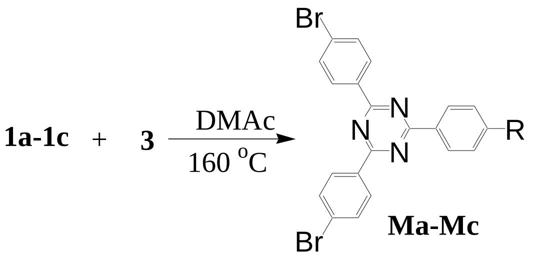
1.2.3 Synthesis of 4-bromobenzamidine hydrochloride, **3**.



3

A solution of **2** (50 mmol) in 150 mL of ethanol was bubbled by dry NH_3 gas for 30 min. Then the mixture was allowed to heat to 60 °C until appearance of a clear solution. After removing the solvent under reduced pressure, **3** was obtained in a yield of 92% as white crystals. ^{1}H NMR (DMSO-d_6)**,** δ 9.43 (2H, s), 9.17 (2H, s), 7.85 (2H, d), 7.74 (2H, d).

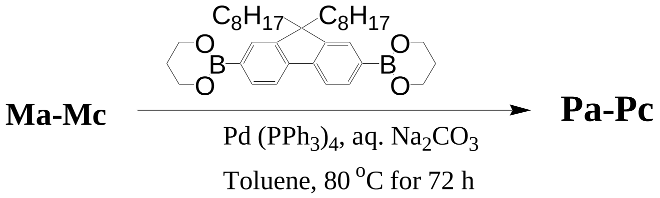
1.2.4 Synthesis of the monomers, **Ma-Mc.**



Ma-Mc

These compounds were prepared by modifying the literature method.[1] Thus, a solution of **3** (50 mmol) and **1a** or **1b** or **1c** (23 mmol) in 50 mL of DMAc was heated to 180 °C and maintained this temperature for 48 h. After being cooled to room temperature, the mixture was added dropwise to 1 L of methanol to give white solid. **Ma-Mc** were obtained after filtration and drying under vacuum. Yield: **Ma**, 23%; **Mb**, 27%; **Mc** 21%. M.p: **Ma**, 262 °C; **Mb**, 287 °C; **Mc**, 241 °C. FT-IR (NaCl pellets, cm^{-1}), **Ma**, 3062, 1581, 1514, 818, 775; **Mb**, 3065, 2850, 1605, 1581, 1518, 1369, 807; **Mc**, 3064, 2904, 1607, 1578, 1513, 1367, 806. ^{1}H-NMR ($CDCl_3$): **Ma**, δ 8.74 (2H, d), 8.63 (4H, d), 7.73 (4H, d), 7.60 (3H, m) **Mb**, δ, 8.69 (2H, d), 8.60 (4H, d), 7.69 (4H, d) , 7.06 (2H, d), 3.93 (3H, s); **Mc**, δ 8.59 (6H, m), 7.68 (4H, d), 6.79 (2H, d), 3.12 (6H, s); MS (EI): **Ma**, m/z 181 (100%), 183 (96.84%), 102 (84.48%), 103 (56.54%), 467 (51.85%), 465 (27.75%), 469 (25.50%), 76 (28.28%), 75 (21.03%), 77 (13.43), 51 (11.89%); **Mb**, m/z 133 (100%), 134 (19.55%), 497 (80.94%), 495 (44.63%), 499 (40.57%), 102 (34.22%), 103 (22.36%), 181 (16.62%), 183 (16.23%), 75 (9.47%), 63 (5.70%), 51 (5.03%); **Mc**, MS (MOLDI-TOF), M^+ 510.

1.2.5 Synthesis of Polymers



To a 250 mL Schlenk tube charged with 0.5 mmol of **Ma** (**Mb** or **Mc**), 0.5 mmol of 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) and 0.05 mmol of $Pd(PPh_3)_4$ was added 100 mL degassed toluene. The mixture was stirred for 30 min at room temperature under argon before 5 mL of 2 M Na_2CO_3 aqueous solution (10 mmol, bubbled by argon through the solution for 0.5 h) was added. The mixture was heated to 80 °C and maintained this temperature for 72 h under intensive stirring. After being cooled to room temperature, the resulting mixture was diluted with 100 mL of toluene. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was re-dissolved in 10 mL of chloroform, and the solution was poured into 200 mL of methanol to give a polymer precipitate. After filtration and drying under vacuum, **Pa** (**Pb** or **Pc**) was obtained as off-white powder. Yields: **Pa**, 55%; **Pb**, 57%; **Pc,** 68%**.** Molecular weight (GPC, eluent = chloroform, detector = R. I): **Pa**, Mn, 5,400, Mw/Mn (PDI), 1.55; **Pb**: Mn, 5,300, Mw/Mn (PDI), 1.91; **Pc**, Mn, 5,500, Mw/Mn (PDI), 1.50. FT-IR (NaCl pellets, cm^{-1}): **Pa**: 3062, 2925, 2852, 1586, 1514, 1368, 816; **Pb,** 3065, 2926, 2852, 1584, 1507, 1371, 810; **Pc**, 3064, 2925, 2852, 1569, 1506, 1362, 808. ^{1}H-NMR ($CDCl_3$): **Pa**, 8.93 (2H, d), 8.85 (4H, d), 7.45-7.95 (13H, m), 2.18 (4H, m), 1.05-1.25 (20H, m), 0.75-0.85 (10H, m); **Pb**, 8.72-8.93 (6H, m), 7.42-8.05 (10H, m), 7.09 (2H, d), 3.97 (3H, s), 2.17 (4 H, m), 0.94-1.35 (20H, m), 0.62-0.94 (10H, m); **Pc**, 8.68-8.92 (6H, m), 7.45-7.93 (10H, m), 6.85 (2H, d), 3.14 (6H, s), 2.18 (4H, m), 1.13 (20H, m), 0.69-0.85 (10H, m). Elemental analysis: **Pa**, Calcd for $Br\text{-}(C_{50}H_{53}N_3\ 0.5H_2O)_8\text{-}B(OH)_2$, C, 83.38%; H, 7.54%; N, 5.84%; Br, 1.39%. Found: C, 83.15%; H, 7.65%; N, 5.20%; Br, 1.11%. **Pb,** Calcd for $Br\text{-}(C_{51}H_{55}N_3O\ 1.6\ H_2O)_7\text{-}B(OH)_{2,}$ C, 79.31%; H, 7.58%; N, 5.44%, Br 1.48. Found: C, 79.23%, H, 7.72%; N, 4.76%; Br, 0.5%. **Pc,** Calcd for $Br\text{-}(C_{52}H_{58}N_4\ H_2O)_7\text{-}B(OH)_2$, C, 80.79%; H, 7.81%; N, 7.26%; Br, 1.48%. Found: C, 80.61%; H, 7.68%; N, 6.92%; Br, 1.99%.

1.3 Measurements

^{1}H NMR spectra were carried out on a Bruker DRX 400 spectrometer, using $CDCl_3$ as solvent and TMS as internal standard. FT-IR spectra were recorded on a Nicolet spectrometer with NaCl pellets. Elemental analysis was taken with a Carlo Erba 1106 elemental analyzer. A Perkin Elmer Series 200 GPC system was employed to deduce a number-average molecular weight (Mn) and molecular weight distribution (Mw/Mn) based on polystyrene as standards. UV-visible absorption spectra were obtained with a Hitachi UV2800 spectrophotometer. Photoluminescence was measured with a Hitachi F-4500 fluorescence spectrophotometer. Thermal stability was determined with a TA 2000 thermogravimetric analyzer at a heating rate 10 ºC min^{-1} in nitrogen. Cyclic voltammetry of cast films of the polymers on Pt plates was performed in an acetonitrile solution of $[Bu_4N]BF_4$ (0.10 M, Bu = butyl)) under argon using (0.10 M $AgNO_3$)/Ag and platinum wire as reference and counter electrodes, respectively. A CHI 600B analyzer (Shanghai Chen Hua Company) was used for the cyclic voltammetry.

2. Characterization and the thermal properties of Pa-Pc

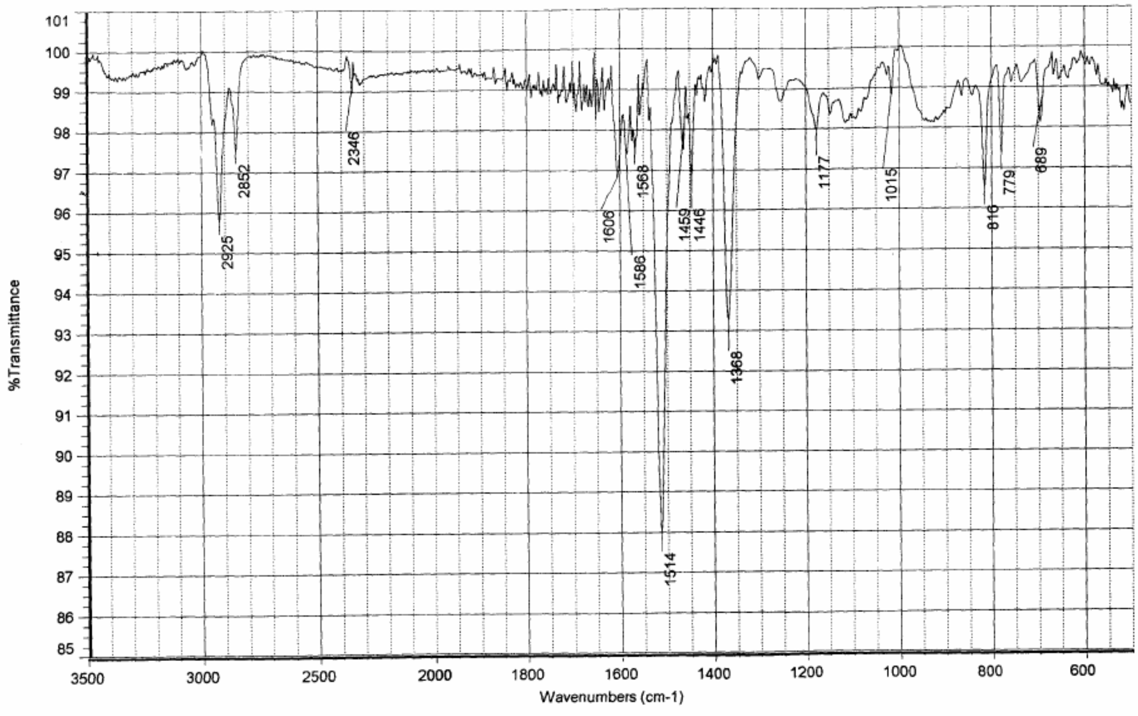


Figure S1. FT-IR spectrum of **Pa.**

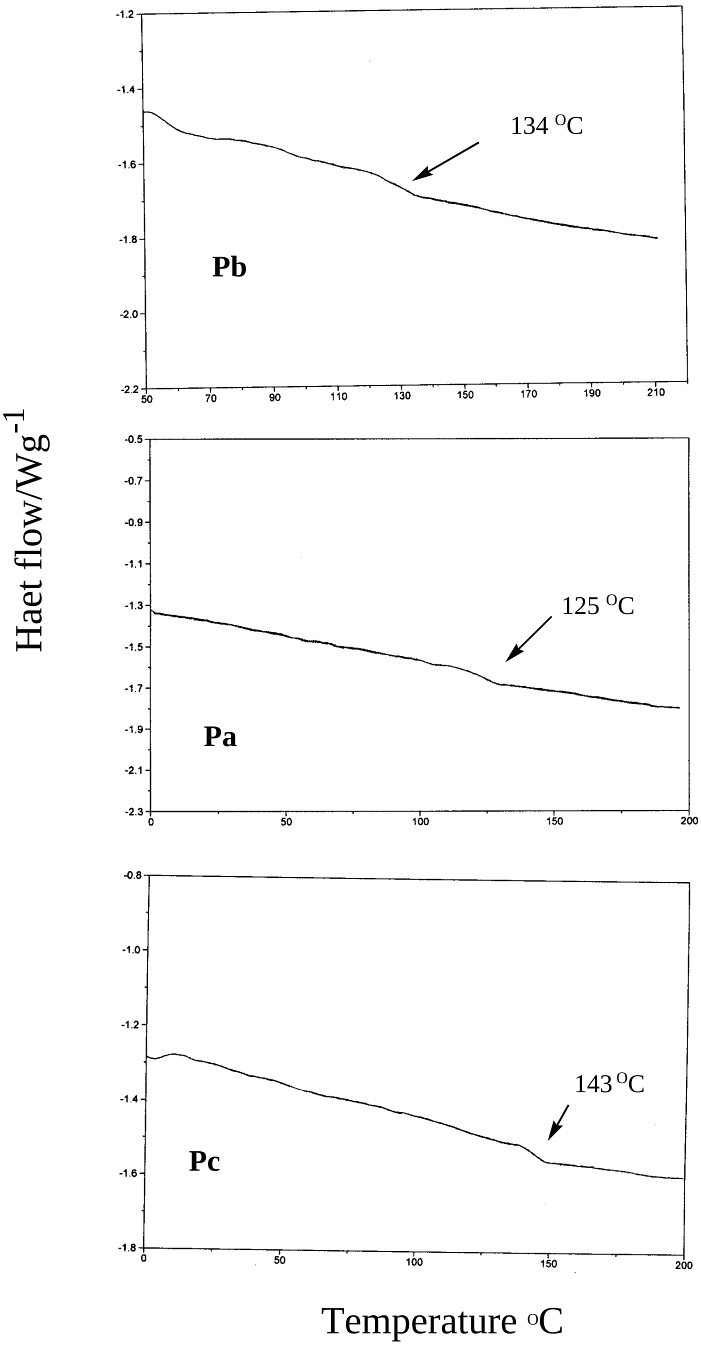


Figure S2. DSC traces of **Pa-Pc.**

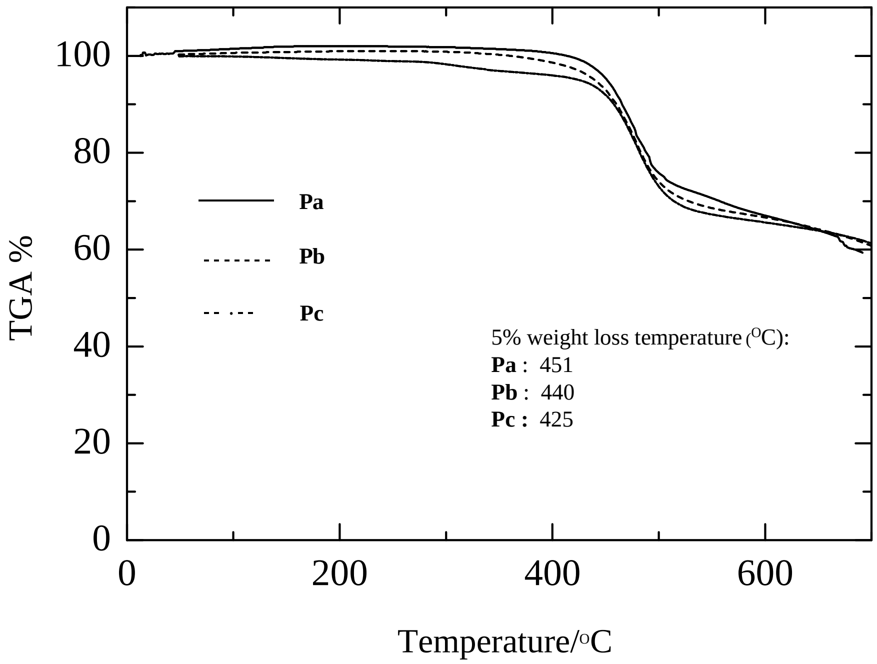


Figure S3. TGA curves of **Pa-Pc.**

Reference

[1] V. P. Borovik, V. P. Mamaev, *Sibirski Khim. Zh.* **1999**, *4*, 96.