Supplementary Information

Tunable Conversion from Saturable Absorption to Reverse Saturable Absorption in Poly (Pyrrole Methine) Derivatives

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1. Materials

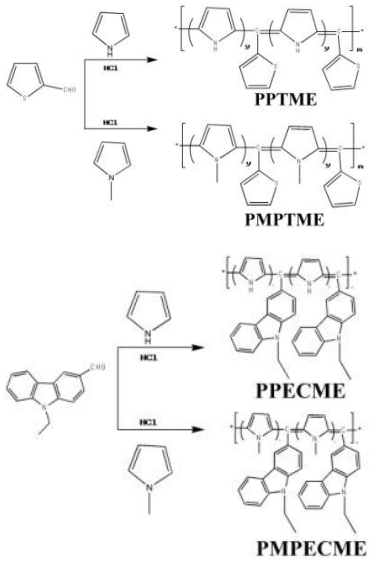
All starting materials were purchased from commercial suppliers and used without further purification.

2. Measurements

The ^{1}H NMR spectra was recorded on an AV III Ascend 500 HD spectrometer. $\overline{M}_n$ was recorded on a waters 1515 GPC.

3. Synthesis

The general route is shown in Scheme S1.



Scheme S1. Synthesis route of four poly (pyrrole methine) derivatives

Synthesis of PPTME

A mixture of pyrrole (0.3354g, 5mmol), 2-thenaldehyde (0.5607g, 5mmol) and 36.5%HCl (wt%) 3 drops were dissolved in 15mL CH_2Cl_2. Under the protection of argon, the solution was stirred at 25℃ for 10 h. After removal of solvent, 2 mol% ammonia was used to neutralize crude product for 6 h. Then crude product was washed with water to neutral and vacuum dryed for 24h. The crude product was purified by silica gel using PET/CH_2Cl_2 as eluent and then vacuum dryed. The resulting polymer is as brown solid in 41.8% yield and characterized by ^{1}H NMR and GPC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01-7.49 (m, 13H), 7.26 – 7.08 (m, 18H), 7.08 – 6.72 (m, 26H), 6.72 – 6.09 (m, 28H), 6.09 – 5.70 (m, 24H), 5.70 – 5.18 (m, 15H), 2.90 – 2.82 (s, 9H). $\overline{M}_n$=2424.

Synthesis of PMPTME

A mixture of 1-methylpyrrole (0.4054g, 5mmol), 2-thenaldehyde (0.5602g, 5mmol) and 36.5%HCl (wt%) 3 drops were dissolved in 15mL CH_2Cl_2. Under the protection of argon, the solution was stirred at 25℃ for 10 h. After removal of solvent, 2 mol% ammonia was used to neutralize crude product for 6 h. Then crude product was washed with water to neutral and vacuum dryed for 24h. The crude product was purified by silica gel using PET/CH_2Cl_2 as eluent and then vacuum dryed. The resulting polymer is as murrey solid in 45.6% yield and characterized by ^{1}H NMR and GPC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 – 6.63 (m, 81H), 6.73 (s, 20H), 6.73 (s, 16H), 6.55 (s, 5H), 5.95 (d, 11H), 5.90 (s, 3H), 5.76 – 5.18 (m, 45H), 3.39 (m, 30H), 3.16 (s, 39H). $\overline{M}_n$=2060.

Synthesis of PPECME

A mixture of pyrrole (0.3350g, 5mmol), N-Ethyl-3-carbazolecarboxaldehyde (1.1164g, 5mmol) and 36.5%HCl (wt%) 3 drops were dissolved in 15mL CH_2Cl_2. Under the protection of argon, the solution was stirred at 25℃ for 10 h. After removal of solvent, 2 mol% ammonia was used to neutralize crude product for 6 h. Then crude product was washed with water to neutral and vacuum dryed for 24h. The crude product was purified by silica gel using PET/CH_2Cl_2 as eluent and then vacuum dryed. The resulting polymer is as brown solid in 39.9% yield and characterized by ^{1}H NMR and GPC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 – 7.39 (m, 13H), 7.38 – 7.27 (m, 16H), 5.37 (s, 2H), 5.32 (s, 2H), 4.46 – 4.19 (m, 10H), 4.19 – 3.24 (m, 10H), 2.96 (s, 2H), 2.89 (s, 2H), 2.78 (d, 12H), 2.91 – 2.02 (m, 18H), 1.55 – 1.14 (m, 57H). $\overline{M}_n$=2050.

Synthesis of PMPECME

A mixture of 1-methylpyrrole (0.4057g, 5mmol), N-Ethyl-3-carbazolecarboxaldehyde (1.1160g, 5mmol) and 36.5%HCl (wt%) 3 drops were dissolved in 15mL CH_2Cl_2. Under the protection of argon, the solution was stirred at 25℃ for 10 h. After removal of solvent, 2 mol% ammonia was used to neutralize crude product for 6 h. Then crude product was washed with water to neutral and vacuum dryed for 24h. The crude product was purified by silica gel using PET/CH_2Cl_2 as eluent and then vacuum dryed. The resulting polymer is as murrey solid in 42.1% yield and characterized by ^{1}H NMR and GPC.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (s, 5H), 7.77 (d, 7H), 7.87 – 6.32 (m, 51H), 6.75 (d, 7H), 6.12 (s, 10H), 6.54 – 5.40 (m, 13H), 5.30 (s, 3H), 4.31 (s, 16H), 3.42 (s, 7H), 3.15 (s, 4H), 2.98 (d, 2H), 2.88 (s, 1H), 2.80 (s, 1H), 3.25 – 1.72 (m, 22H), 2.11 (d, 10H), 1.49 – 1.27 (m, 47H). $\overline{M}_n$=1841.