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Supporting Information to:

Cationic Polymerization of Dibenzofulvene Leading to a π -Stacked Polymer

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Fig. S1. IR spectra (full range) of poly(DBF)s prepared by anionic (a), radical (b), and cationic (c) polymerizations. [THF-insoluble polymers, KBr pellet]

Fig. S2. MALDI-TOF mass spectra of THF-soluble poly(DBF)s prepared using $\text{BF}_3\text{-Et}_2\text{O}$ (run 10 in Table 1) and (A) and using $\text{CH}_3\text{SO}_3\text{H}$ (run 11 in Table 1) (B). Samples were prepared by depositing $1\mu\text{L}$ of poly(DBF) solution in CHCl_3 (7 mg/mL) onto pre-formed thin layer of dithranol matrix by drop-casting $1\mu\text{L}$ of THF solution (10 mg/mL, 4.42×10^{-2} M) in a sample well.

Fig. S3. ^1H NMR spectra of poly(DBF) prepared using $\text{BF}_3\text{-Et}_2\text{O}$ (run 10 in Table 1) before (a) and after heat treatment in CDCl_3 solution at 60°C for 0.5 h (b), 1 h (c), 3 h (d), and 6 h (e). [400 MHz, CDCl_3 , 23°C]

Fig. S4. ^1H NMR spectra (aromatic region) of poly(DBF) samples prepared by cationic polymerization using $\text{BF}_3\text{-OEt}_2$ in CH_2Cl_2 at 0°C (run 3 in Table 1) and isolated by preparative SEC: M_n 1430 (a), 1000 (b), 920 (c), 820 (d), and 740 (e). [400 MHz, r.t., CDCl_3]

Fig. S5. Analytical SEC profiles of poly(DBF) samples prepared by cationic polymerization using $\text{BF}_3\text{-OEt}_2$ in CH_2Cl_2 at 0°C (run 3 in Table 1) and isolated by preparative SEC.