# Synthetic route to conjugated donor-acceptor polymer brushes via alternating copolymerization of bifunctional monomers

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**SUPPORTING INFORMATION**

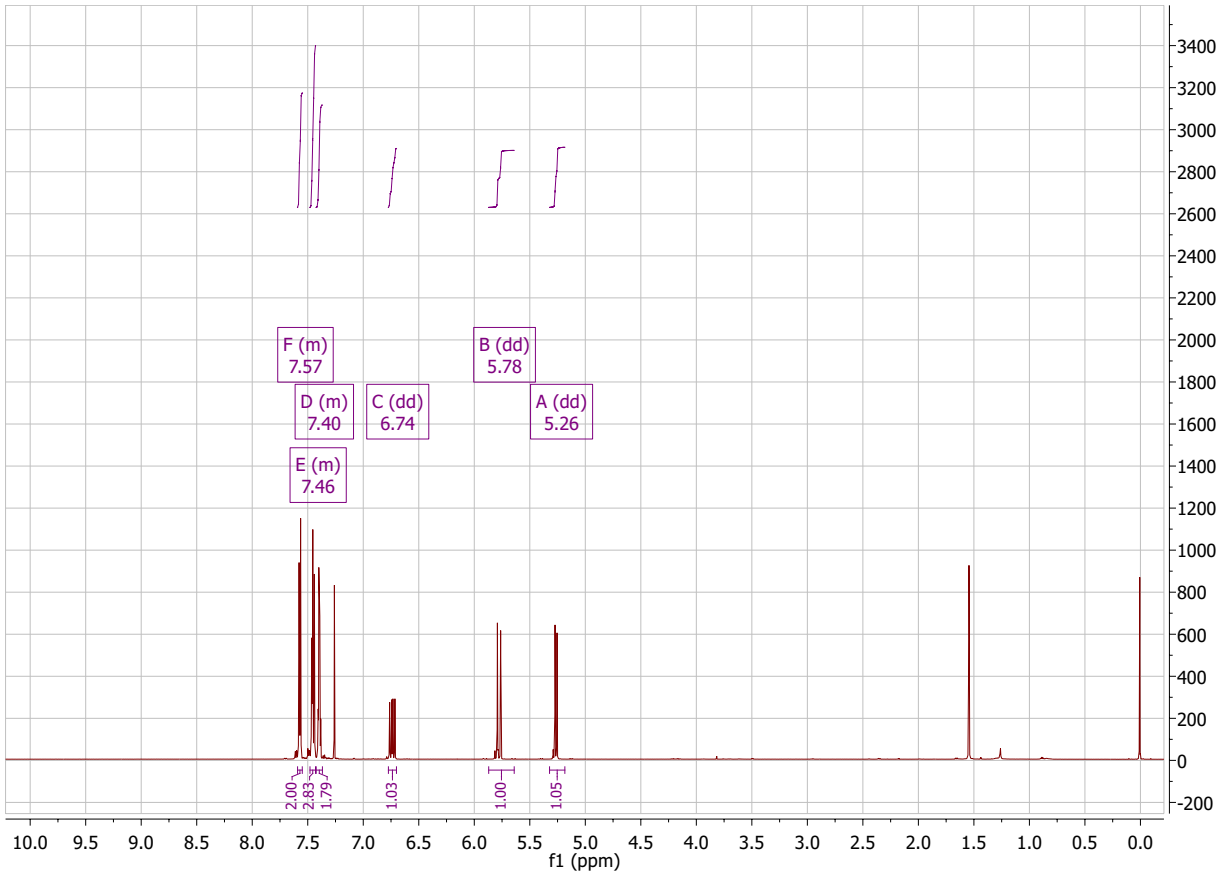


**Figure S1.** The [1]H NMR spectrum of synthesized donor **St-D** monomer.

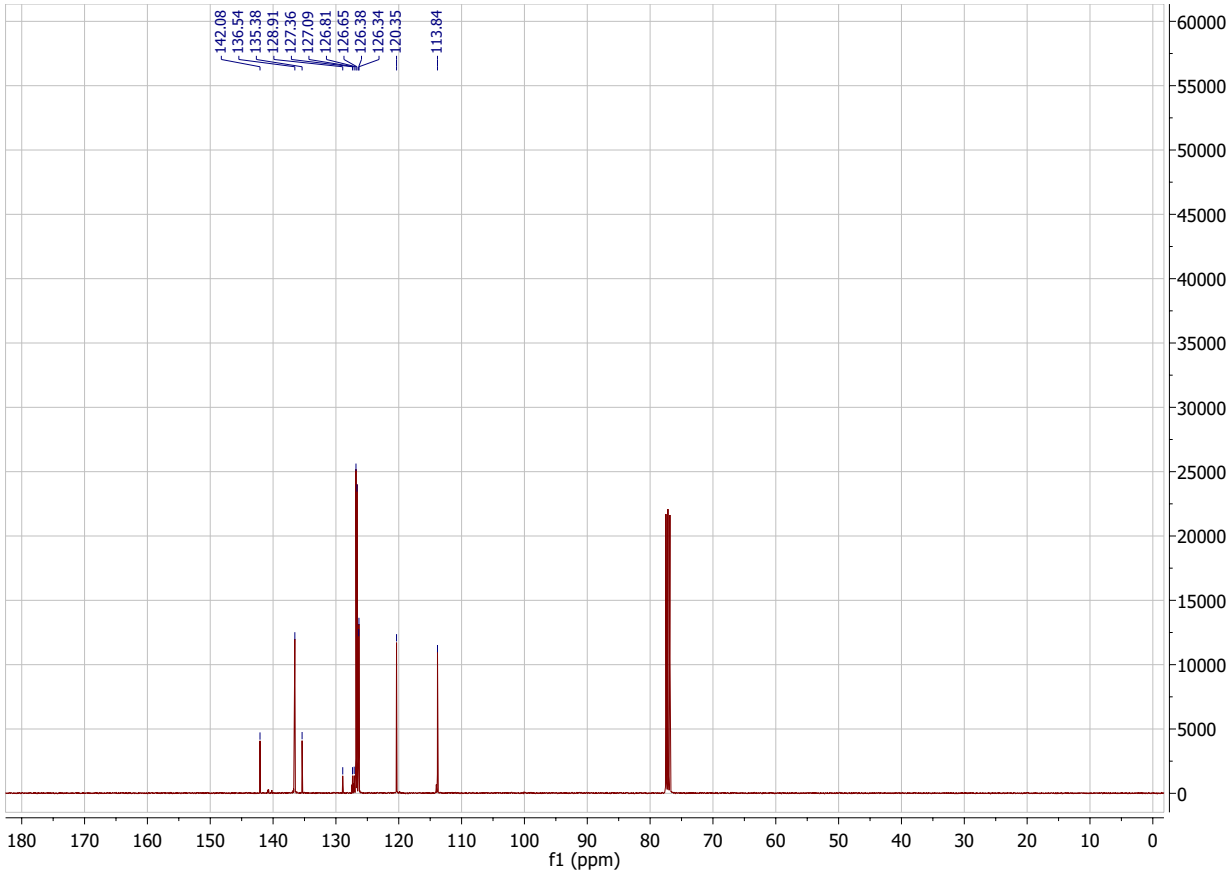


**Figure S2.** The $^{13}C$ NMR spectrum of synthesized donor **St-D** monomer.

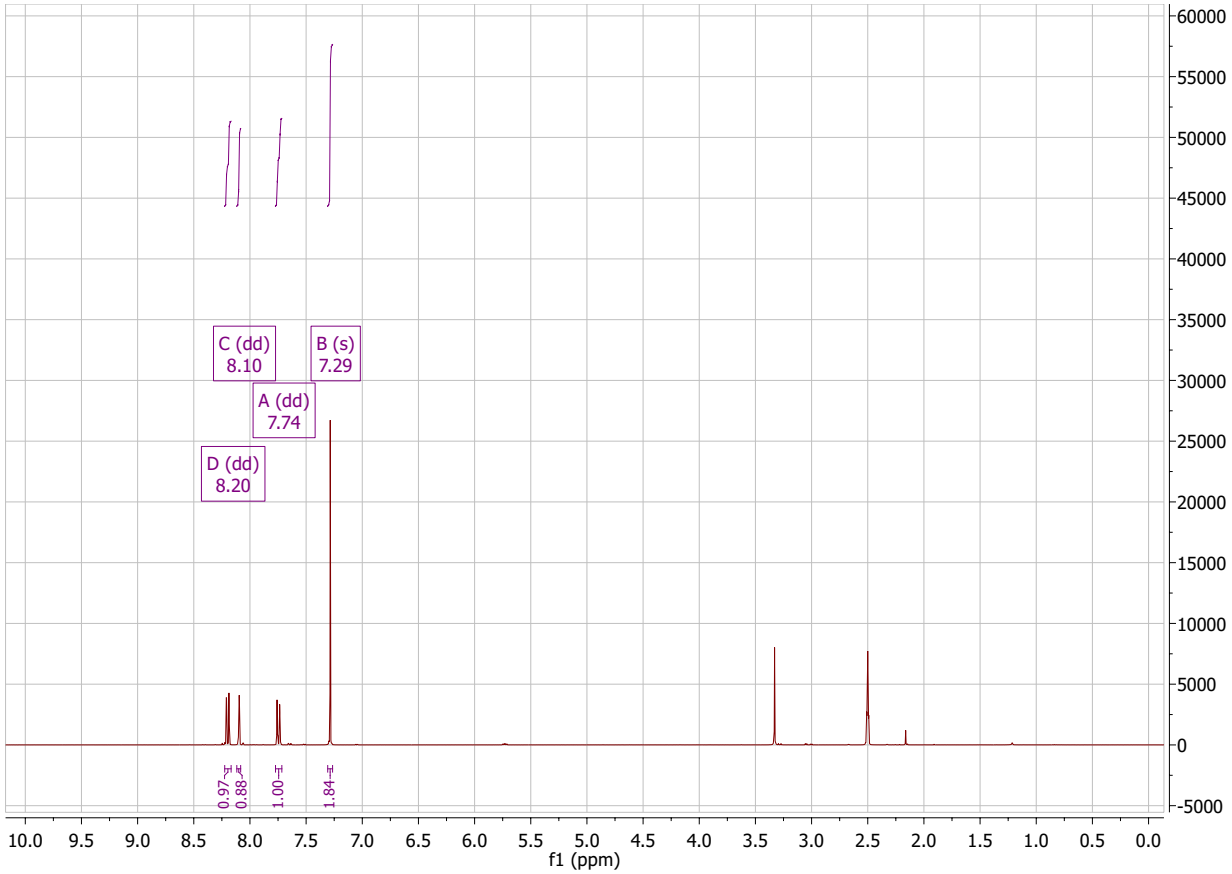


**Figure S3.** The $^{1}$H NMR spectrum of synthesized acceptor **Ma-A** monomer.

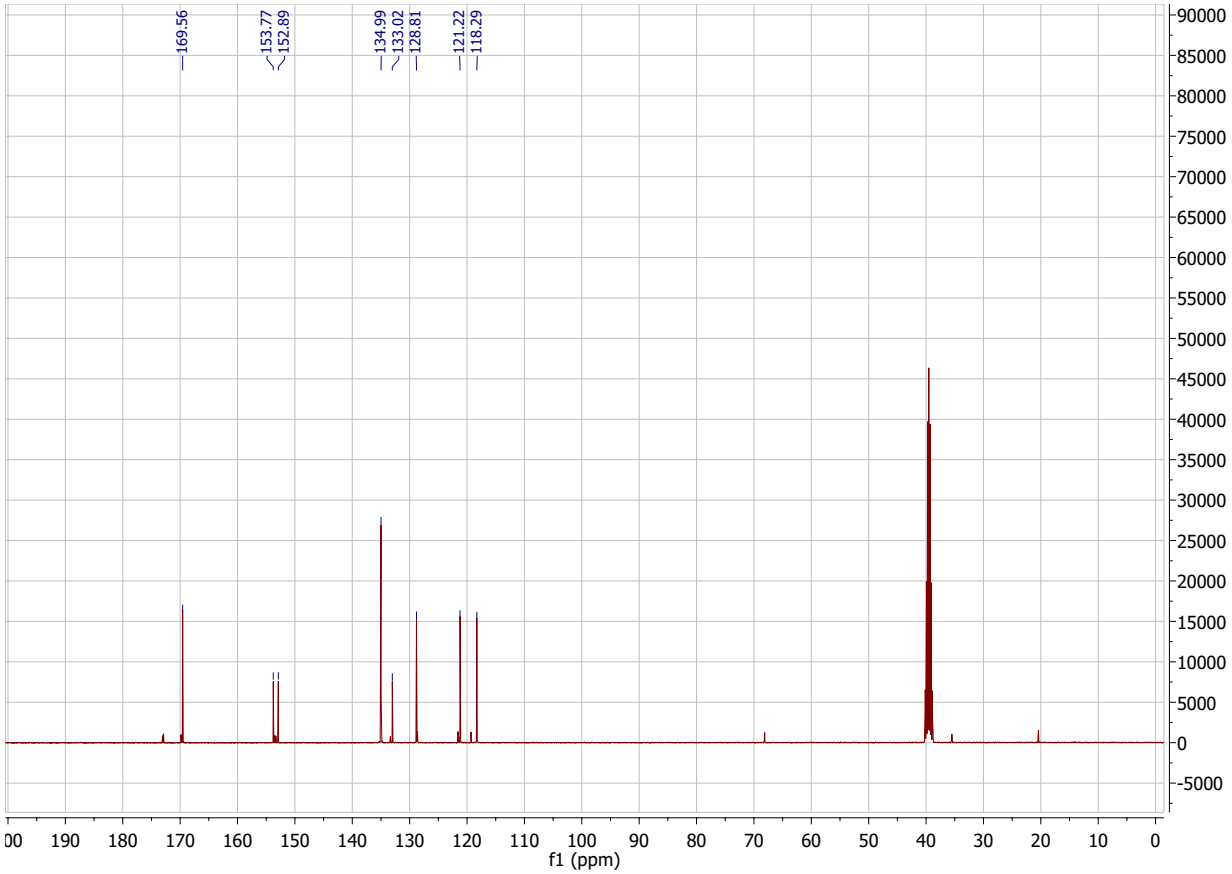


**Figure S4.** The $^{13}C$ NMR spectrum of synthesized acceptor **Ma-A** monomer.

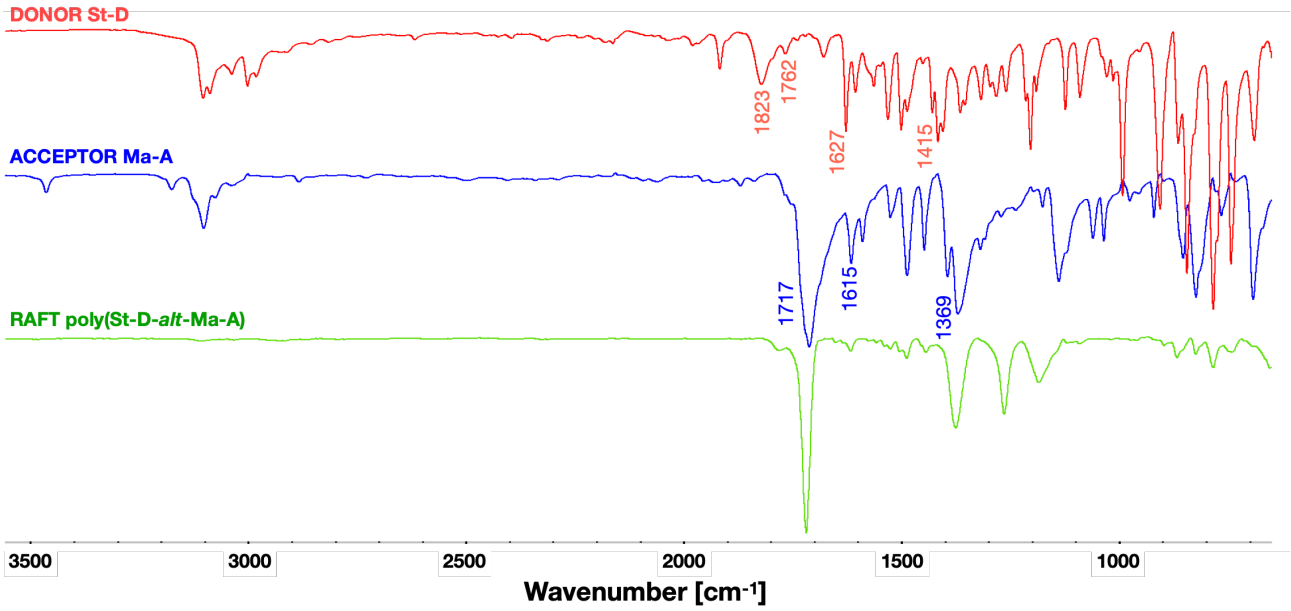


**Figure S5.** The IR transmittance spectra of synthesized donor and acceptor monomers, as well as the polymer brushes obtained via surface-initiated RAFT polymerization.
Donor (**St-D**): 1415 $cm^{-1}$ (C=C stretching vibrations in thiophene ring), 1627 $cm^{-1}$ (C=C stretching vibrations), 1823 and 1762 $cm^{-1}$ (C=C overtones of stretching vibrations in benzene ring);
Acceptor (**Ma-A**): 1369 $cm^{-1}$ (C=N stretching vibrations in benzo[c][1,2,5]thiadiazol ring), 1615 $cm^{-1}$ (C=C stretching vibrations), 1717 $cm^{-1}$ (C=O stretching vibrations in carbonyl group).

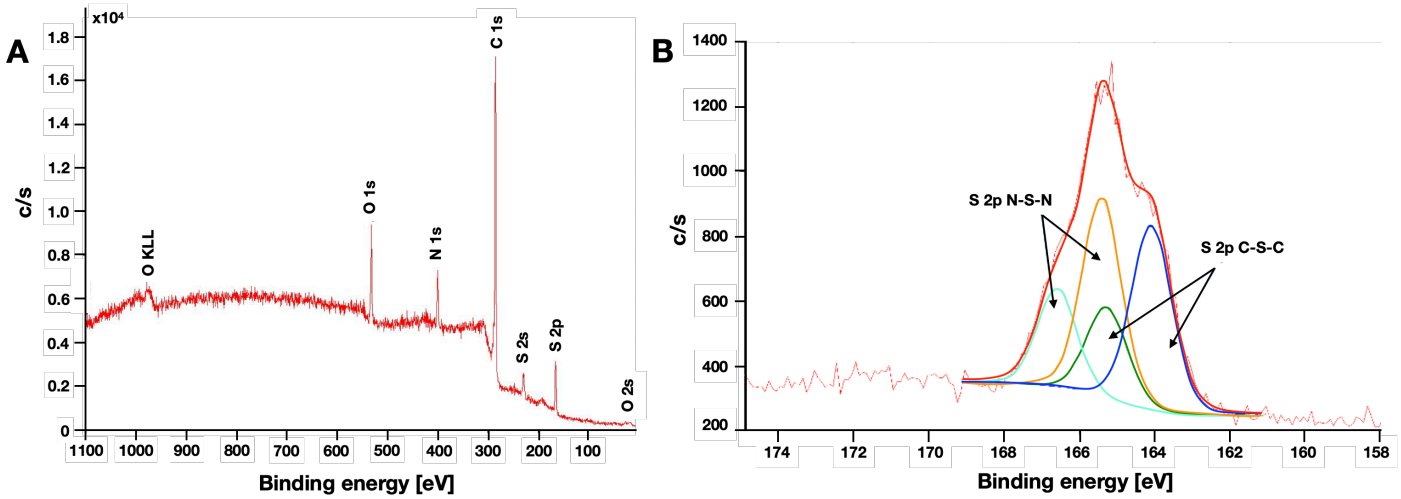


**Figure S6.** The XPS spectrum of (**A**) poly(**St-D**-*alt*-**Ma-A**) brushes obtained via RAFT polymerization and (**B**) sulfur region.

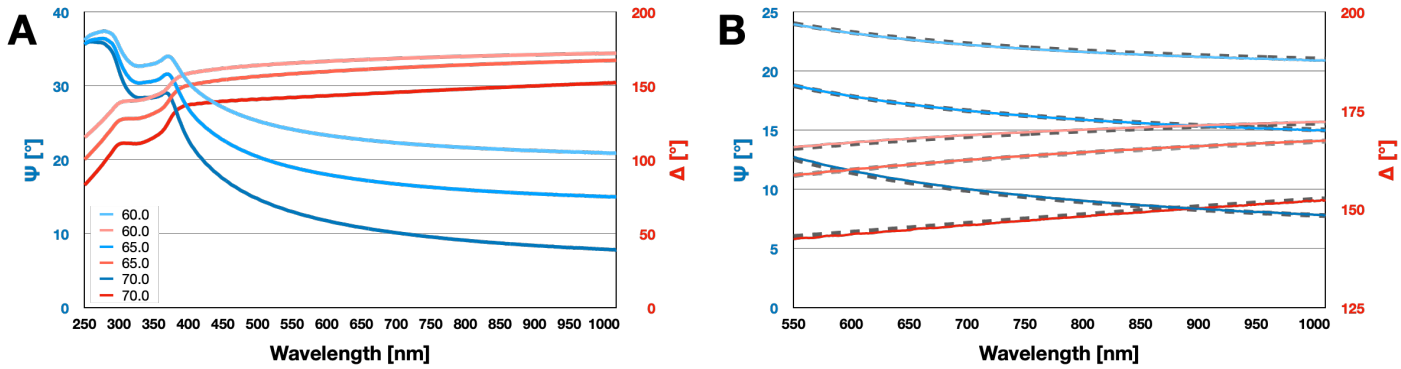


**Figure S7.** Exemplary spectroscopic ellipsometry data for the polymer brushes obtained via RAFT polymerization (**A**) and their fits to the Cauchy model (**B**).

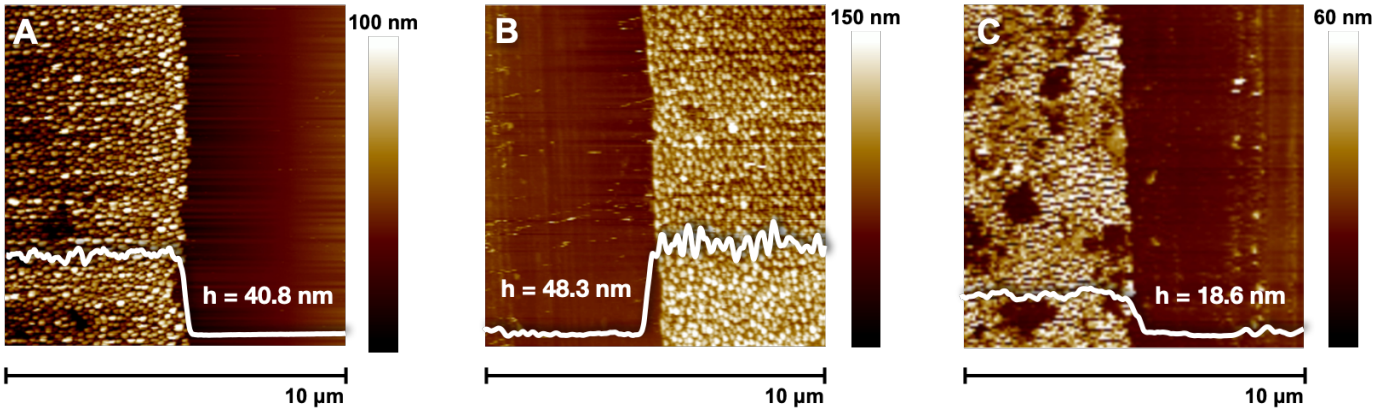


**Figure S8.** AFM pictures of poly(**St-D**-*alt*-**Ma-A**) brushes obtained via RAFT polymerization with various grafting densities: (**A**) 100% (**B**) 80% and (**C**) 70%.

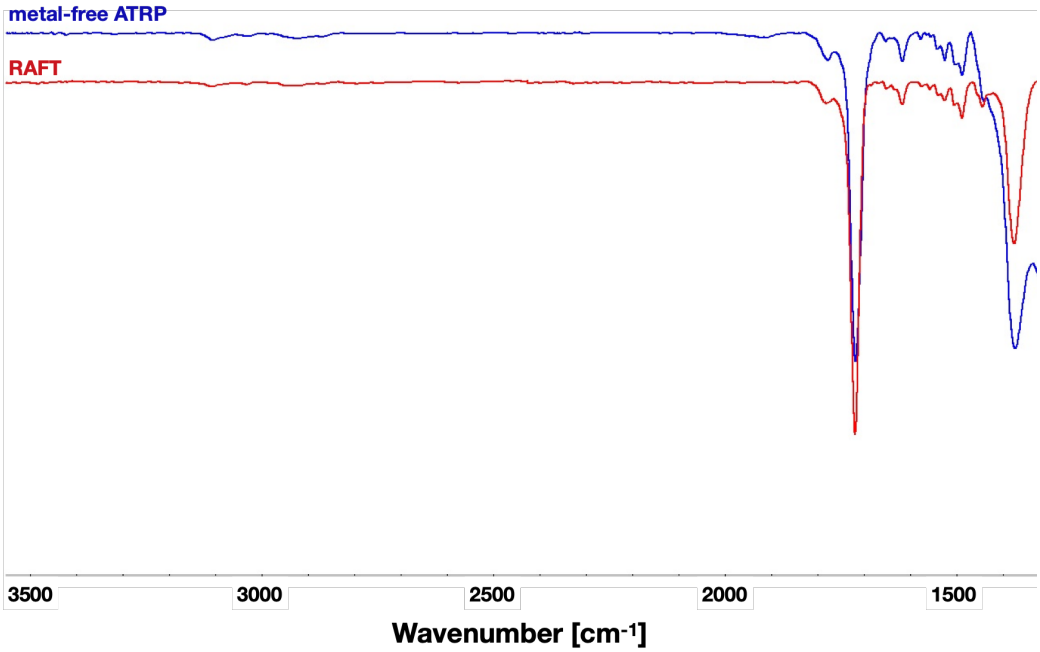


**Figure S9.** The IR transmittance spectra (1300 – 3500 $cm^{-1}$) of poly(**St-D**-*alt*-**Ma-A**) brushes obtained via RAFT and metal-free ATRP (the spectra at wavenumbers below 1300 $cm^{-1}$ contain some artefacts related to the ITO substrates and are not comparable).

**Table S1.** Thickness of donor-acceptor brushes obtained during various time of metal-free ATRP polymerization

| Polymerization time [h] | Brush thickness based on spectroscopic ellipsometry [nm] | Brush thickness based on AFM [nm] |
|---|---|---|
| 0.75 | 3.5 ± 0.0 | - |
| 1.50 | 5.8 ± 0.1 | 5.1 ± 0.1 |
| 3.00 | 8.5 ± 0.1 | 9.8 ± 0.1 |
| 4.00 | 13.5 ± 1.2 | 13.4 ± 0.2 |
| 6.00 | 22.9 ± 0.3 | 26.9 ± 0.6 |

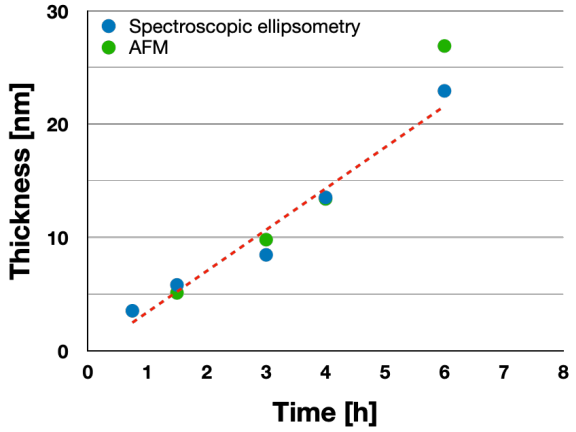


**Figure S10.** The relationship between thickness of donor-acceptor poly(**St-D**-*alt*-**Ma-A**) brushes and time of metal-free ATRP polymerization.

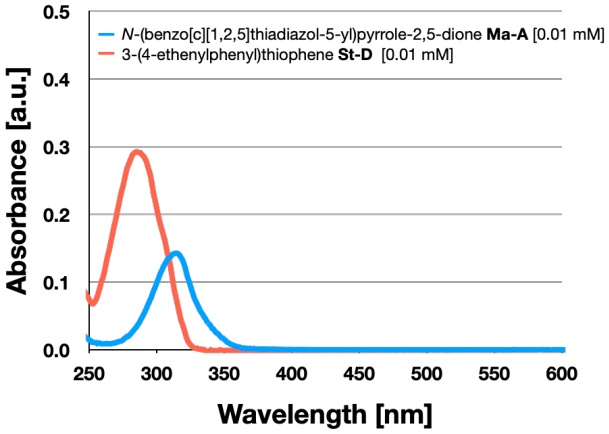


**Figure S11.** UV-Vis absorption spectra of the monomers used to synthesis of donor-acceptor polymer brushes. Solutions of both compounds are prepared in dioxane.