Direct Synthesis of Light-Emitting Triblock Copolymers from RAFT Polymerization

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Supplementary Information

S1. NMR analyses

Figure S1 shows ^{1}H-NMR spectra of distyryl-endcapped PFO **2**. Despite the polymeric nature of this precursor, the signals are quite well defined and do not significantly broaden. We determined the number average molecular weight using end-group analysis[1,2]. Comparing the integrals of the signals of the vinylic protons with those corresponding to the 12,12' and 13.13' protons gives an estimate for the number average molecular weight: ~17.000 g/mol (main text, Figure 2, left-most black symbol).
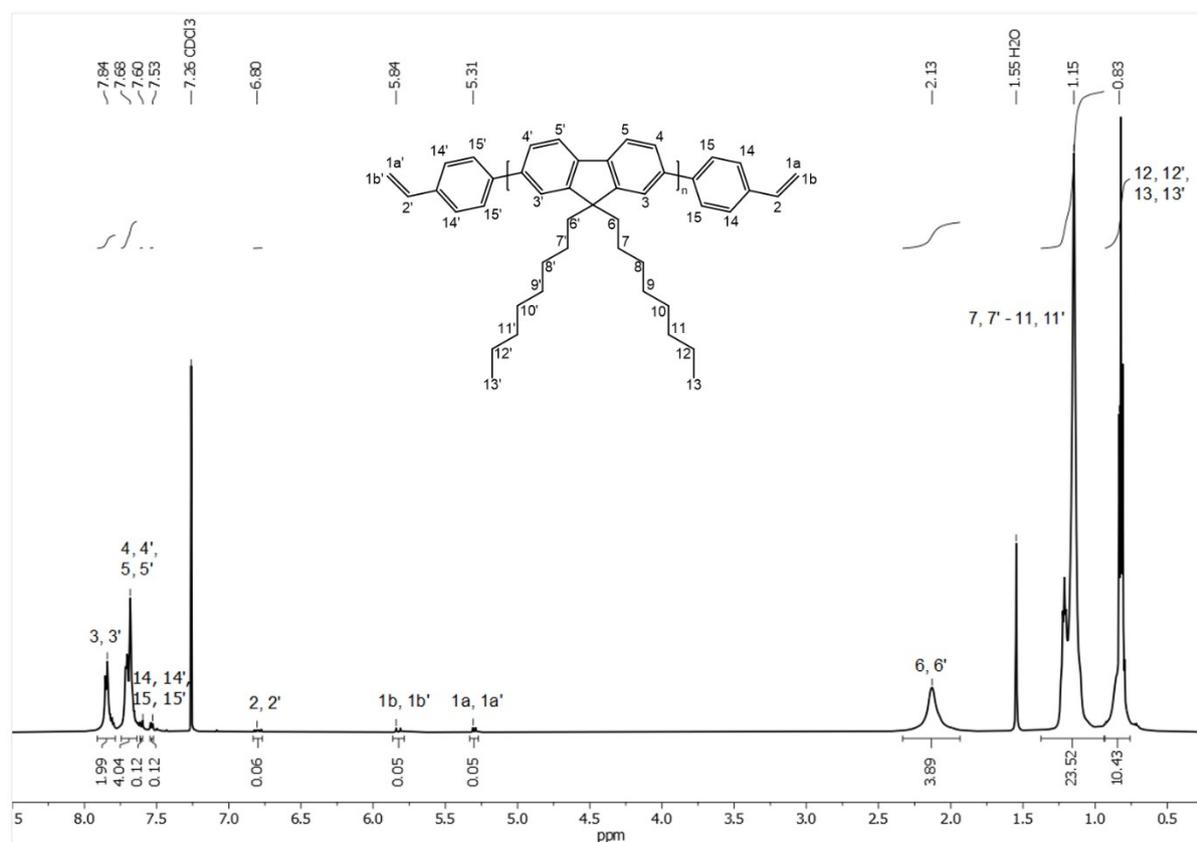

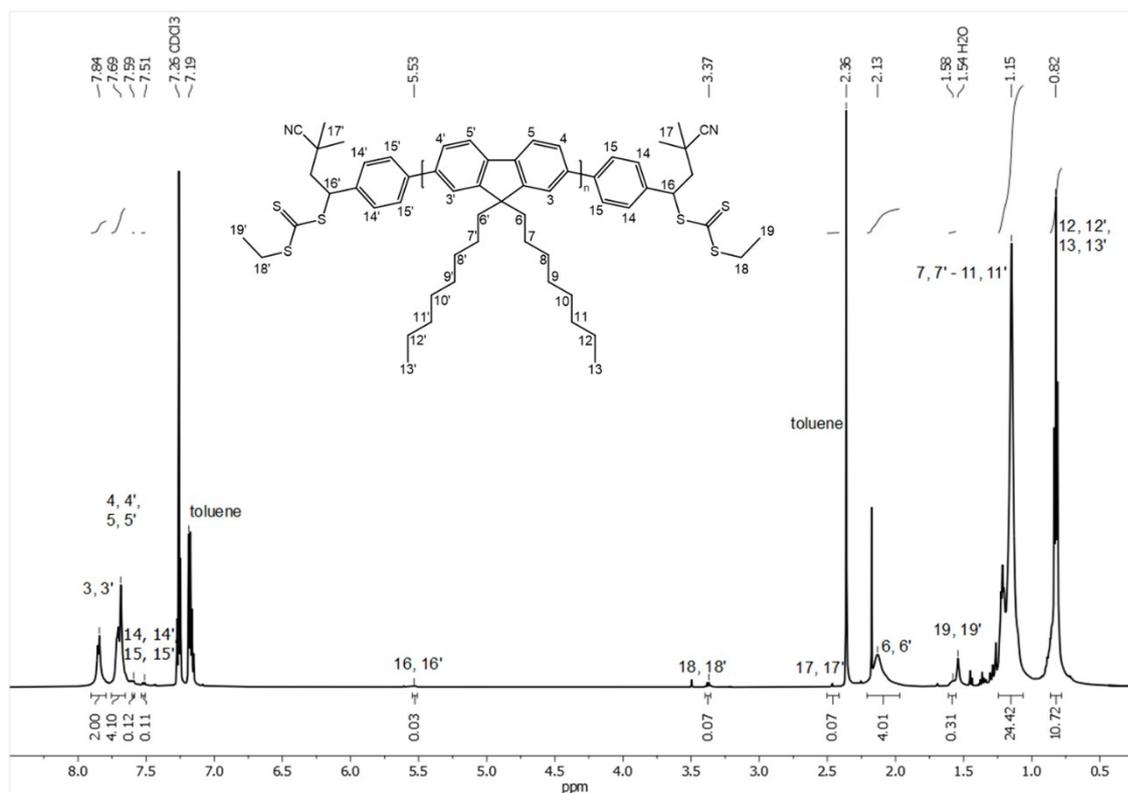***Fig. S1*** *^{1}H NMR spectrum (CDCl₃, 600 MHz) of distyrene-endcapped PFO homopolymer **2**.*

Fig. S2 ^{1}H NMR spectrum (CDCl$_3$, 600 MHz) of di-CPETTC-PFO **3**.

Figure S3 shows ^{1}H-NMR spectra (aliphatic region) taken at subsequent time intervals during the synthesis of PS-b-PFO-b-PS **4**. Based on these spectra, we estimated the number-average molecular weight of the tri-BCP as a function of reaction time (black symbols in main text Figure 2) by comparing the integral of the signal corresponding to position B,B', as indicated in the structure, with the ones associated with positions 12,12' and 13,13' on the side chains of the fluorene monomer (see Figure S2).
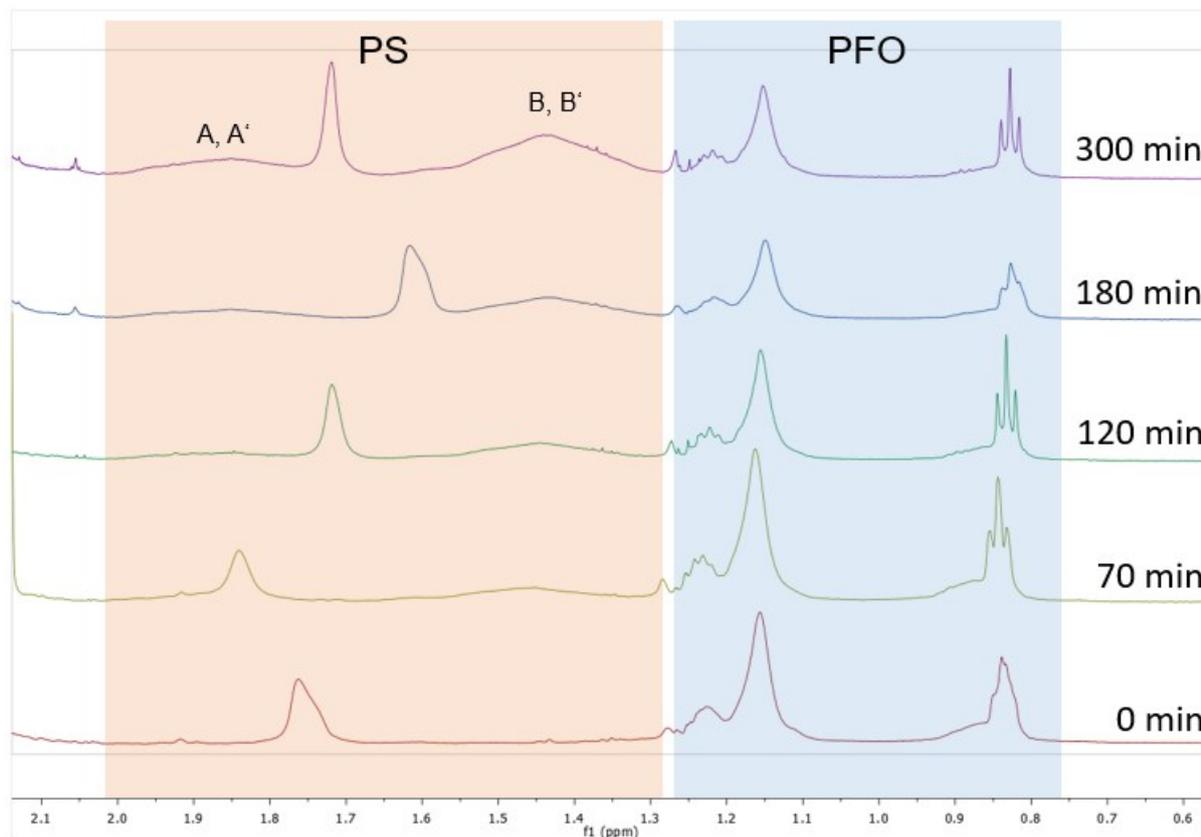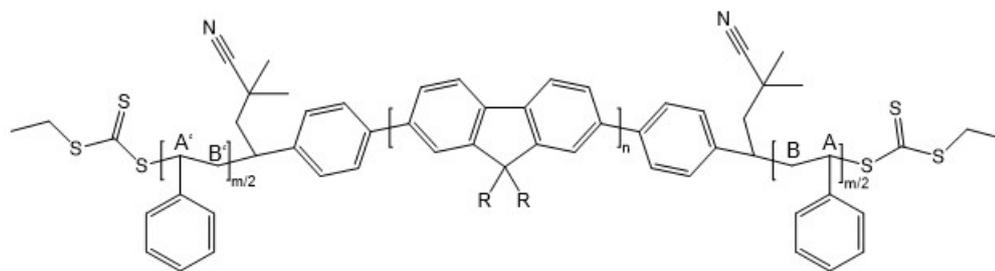
Fig. S3 *^{1}H NMR spectra (CDCl$_3$, 600 MHz) used for kinetic analyses of the RAFT polymerization of PS-b-PFO-b-PS **4** with VAZO88 as initiator.*

The signal at 1.6 – 1.8 ppm is consistent with residual water in the deuterated chloroform[3]. The shifting back and forth of this peak in the spectra for various reaction times may be due to slight changes in polarity and water concentration.

S2. Photoluminescence quantum yield (PLQY) determination

We determined solution PLQYs of tri-BCP **4** and distyryl-endcapped PFO **2** to rule out possible PL quenching by the CPETTC end functionality in the former. For this we used the integrating sphere (absolute) procedure as described previously by Monkman *et al.*[4]. We prepared dilute solution of both samples in toluene and made sure that the optical density of the solution remained below 0.1. The quantum yields were determined to be 48 and 42%, for polymers **4** and **2**, respectively. The similarity between these numbers shows that the RAFT functionalities do not quench the PL of the PFO block. For completeness, we have plotted the normalized PL spectra in Figure S4.
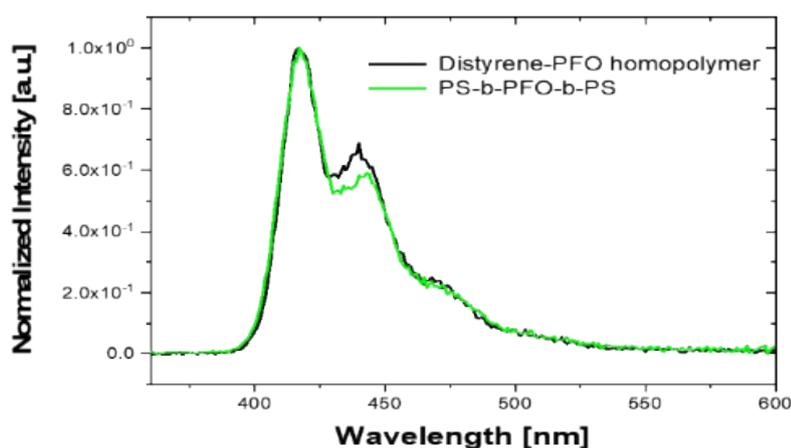

Fig. S4 *Normalized PL spectra of distyrtl-endcapped PFO 2 (black curve) and tri-BCP PS-b-PFO-b-PS 4 (green curve) in toluene.*

[1] Z.-X. Zhang, X. Liu, F. J. Xu, X. J. Loh, E.-T. Kang, K.-G. Neoh and J. Li, Macromolecules 2008, **41**, 5967–5970.

[2] L. Jiang, S. S. Liow and X. J. Loh, Polym. Chem., 2016, **7**, 1693-1700.

[3] https://webspectra.chem.ucla.edu/NotesOnSolvents.html (last visited 10.11.2020)

[4] L. Porrès, A. Holland, L. –O. Pålsson, A. P. Monkman, C. Kemp and A. Beeby, *J. Fluoresc.*, 2006, **16**, 267-272.