

Supporting information for:

# Supramolecular Semifluorinated Dendrons Glued from Weak Hydrogen-Bonds

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## Materials

All chemicals were purchased from Alfa Aesar or Sigma-Aldrich. 2,2,2-trifluoroethyl acrylate (TFEA) was purified by vacuum distillation at room temperature. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from ethanol. Unless otherwise indicated the other chemicals were used without further purification. The chain transfer agent, DAP, was synthesized according to our previous report.<sup>[1]</sup>

## Characterization methods

<sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded on a Varian unity Inova 500 (500 MHz) NMR spectrometer using CDCl<sub>3</sub> as solvent.

Polymers were analyzed by size exclusion chromatography (SEC), running in THF at 35°C (flow rate: 1 mL·min<sup>-1</sup>) and recorded on a GPCmax VE 2001 from Viscotek™, equipped with a column set of a H<sub>HR</sub>-H Guard-17369 column, a CLM30111 column and a G2500H<sub>HR</sub>-17354 column. The number-average molecular weight of all the polymers was derived from a calibration curve based on polystyrene using UV signal.

Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) measurements were performed on a Bruker Autoflex III system (Bruker Daltonics) operating in linear mode. Data evaluation was carried out on DataAnalysis software. Ions were formed by laser desorption (smart beam laser at 355, 532, 808, and 1064 ± 5 nm; up to 50 Hz repetition rate), accelerated by a voltage of 20 kV and detected as positive ions. Samples were prepared by mixing 50 µL of 2,5-dihydroxybenzoic acid at 20 g·L<sup>-1</sup> in THF with 10 µL of polymer solution at 20 g·L<sup>-1</sup> in THF. To enhance cationization of the polymers, 1 µL of NaI at 10 g·L<sup>-1</sup> in acetone

was added to the solutions. Finally, 1  $\mu\text{L}$  of the resulting mixture was spotted on a MALDI sample plate and air-dried.

Rheology experiments were carried out on a rheometer from Anton Paar (Physica) MCR 101/SN 80753612. A parallel plate system with a plate diameter of  $\sim 8$  mm diameter was used. The sample temperature was controlled by thermoelectric heating/cooling in a Peltier-chamber under an atmosphere of dry oxygen. The samples were annealed at  $50$   $^{\circ}\text{C}$  for approximately 10 h prior the rheology experiments. All measurements were performed in a dynamic mode with an angular frequency ranging from 0.01 to 100 rad/s. Frequency sweep measurements were performed within the linear viscoelastic (LVE) region between  $100$   $^{\circ}\text{C}$  to  $0$   $^{\circ}\text{C}$  in  $10$   $^{\circ}\text{C}$  steps whereas samples were equilibrated at least 15 minutes at each temperature. For the evaluation of data the Rheoplus software and OriginPro 8G were used.

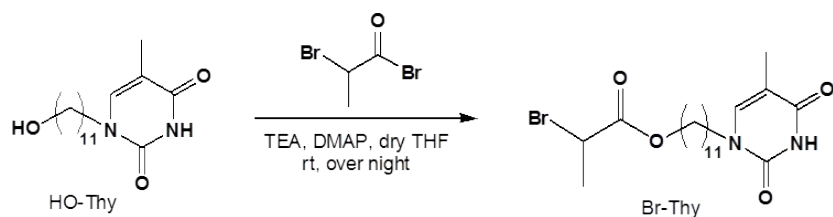
Transmission electron microscopy (TEM) analyses were conducted with an EM 900 transmission electron microscope (Carl Zeiss Microscopy GmbH, Oberkochen, Germany). The samples were dissolved in a suitable solvent (THF or toluene) with a concentration of 2 g/L and spread onto a Cu grid coated with a Carbon-film. After 1 min, excess solution was blotted off with filter paper, afterwards  $\sim 5$   $\mu\text{L}$  of 1% aqueous uranyl acetate solution were deposited onto the grid and drained off after 1 min. TEM images were taken from these negatively stained samples, using a SSCCD SM-1k-120 camera (TRS, Moorenweis, Germany).

Dynamic light scattering (DLS) measurement was conducted in toluene solution at a concentration of 2 g/L on a Viscotek 802 using OmniSIZE software.

## Polymerization of TFEA

Solution polymerization of TFEA was carried out using DAP as chain transfer agent and AIBN as initiator. Typically, solution polymerization of TFEA (1.79 mL,  $1.0 \times 10^{-2}$  mol) was carried out using AIBN (1.64 mg,  $1.0 \times 10^{-5}$  mol), DAP (29.0 mg,  $1.0 \times 10^{-4}$  mol) and DMF (2.0 mL), both as solvent and also as internal reference for the measurement of HFBA consumption via  $^1\text{H}$  NMR. A stock solution was typically transferred into a flask sealed with rubber septum, deoxygenated by nitrogen bubbling for  $\sim 30$  min at  $0^\circ\text{C}$ , then immersed in an oil bath thermostated at  $65^\circ\text{C}$ . The reaction was stopped by plunging the flask into liquid nitrogen. The polymer was subsequently precipitated twice into MeOH/ $\text{H}_2\text{O}$  (1/1, v/v) in order to eliminate residual monomer. The polymer was dried under vacuum and characterized by  $^1\text{H}$  NMR,  $^{19}\text{F}$  NMR and SEC. The molar mass of pure poly(TFEA) was finally evaluated by  $^1\text{H}$  NMR ( $\text{THF-d}_8$ ) from relative integration of the characteristic ester group protons of the PTFEA backbone ( $-\text{O}-\text{CH}_2-\text{CF}_2-$ ,  $2n\text{H}$ ,  $\delta = 4.68$  ppm, with  $n$  being the degree of polymerization) and of the characteristic aromatic protons of DBTTC ( $\text{pH}$ ,  $10\text{H}$ ,  $\delta = 7.12-7.30$  ppm).

## Synthesis of Br-Thy

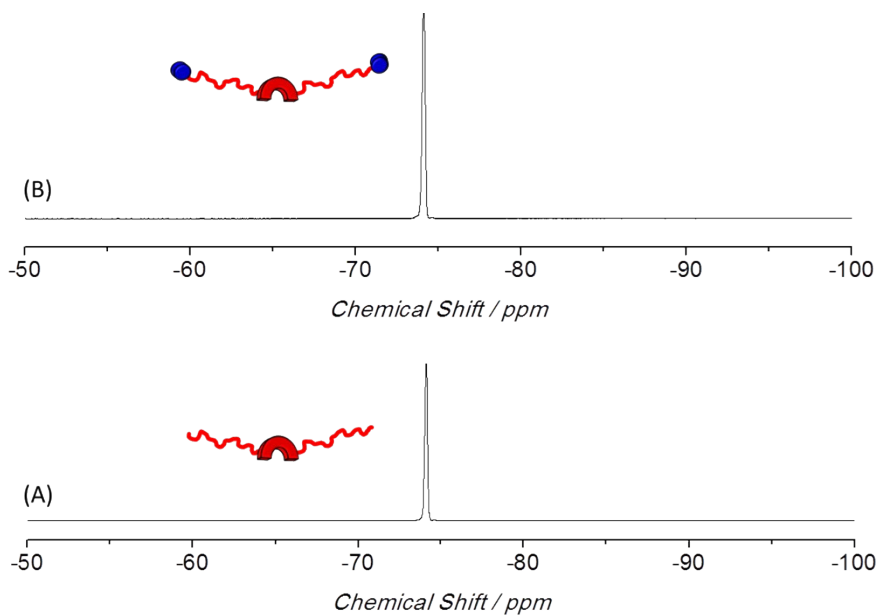


**Figure S1:** Synthetic route to compound Br-Thy.

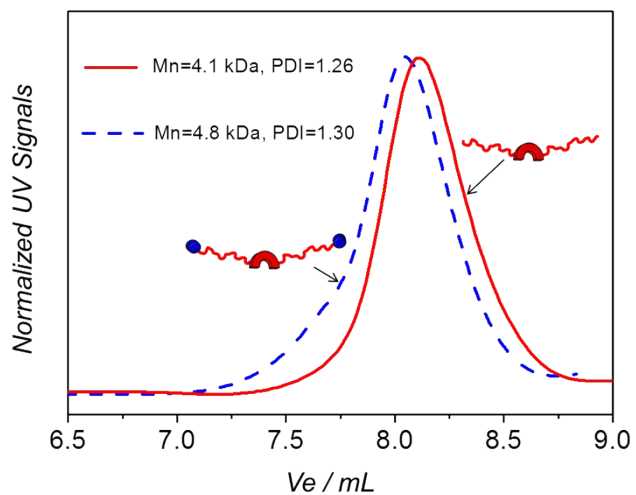
The synthesis of compound Br-Thy was accomplished according to previous report with slight modifications (**Figure S1**).<sup>[2a, 2b]</sup> To a solution of HO-Thy<sup>[1, 3]</sup> (2.5 g, 8.4 mmol), triethylamine (1.3 g, 12.7 mmol) and 4-dimethylaminopyridine (DMAP, 0.5 g, 4.2 mmol) in anhydrous THF (60 mL), an excess of 2-bromopropionyl bromide (2.74 g, 12.7 mmol) was added dropwise. The solution was stirred overnight at room temperature. Then dichloromethane was added into the solution, which was successively washed with saturated sodium bicarbonate, brine and H<sub>2</sub>O. The organic layer was dried over MgSO<sub>4</sub> and the crude product was purified by silica column chromatography (eluent: ethyl acetate/cyclohexane, 1/3, v/v) to give compound Br-Thy as a white solid (2.6 g, 73%) <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 1.26 (br, 16H), 1.65 (quint, 4H), 1.82 (d, 3H), 1.91 (d, 3H), 3.67 (t, 2H), 4.14 (m, 2H), 4.34 (quart, 1H), 6.97 (s, 1H), 8.96 (s, 1H).

### Synthesis of Thy-PTFEA-DAP-PTFEA-Thy

Thy-PTFEA-DAP-PTFEA-Thy was prepared according to literature methods with modifications.<sup>[4a, 4b, 4c]</sup> PTFEA-DAP-PTFEA ( $M_n$  NMR = 4.5 kDa,  $M_n$  SEC = 4.9 kDa,  $\bar{D}$  = 1.20, 45.0 mg, 0.01 mmol), Br-Thy (12.9 mg, 0.03 mmol) and triethylamine (3.0 mg, 0.03 mmol) were dissolved in 0.5 mL acetonitrile and purged with N<sub>2</sub> at room temperature for ~30 min. A solution of hexylamine (2.2 mg, 0.022 mmol) in 0.2 mL of acetonitrile, was added slowly into the above solution under N<sub>2</sub> at room temperature. After 2 hours, the solution was precipitated in cold methanol/H<sub>2</sub>O (2/1, v/v) and then purified by silica column chromatograph (acetonitrile/dichloromethane, 1/9, v/v). The obtained product Thy-PTFEA-DAP-PTFEA-Thy was analyzed by <sup>1</sup>H NMR (**Figure 2**, top), <sup>19</sup>F NMR (**Figure S2**), SEC (**Figure S3**) and MALDI-TOF MS (**Figure 3A, B**, and **Table S2**).



**Figure S2:**  $^{19}\text{F}$  NMR of PTFEA-DAP-PTFEA (A), and Thy-PTFEA-DAP-PTFEA-Thy (B) recorded in  $\text{CDCl}_3$  at  $27^\circ\text{C}$ .



**Figure S3:** Evolution of SEC traces PTFEA-DAP-PTFEA and Thy-PTFEA-DAP-PTFEA-Thy, detector: UV, eluent: THF.

## MALDI-TOF MS results

**Table S1:** MALDI-TOF MS results of PTFEA-DAP-PTFEA.

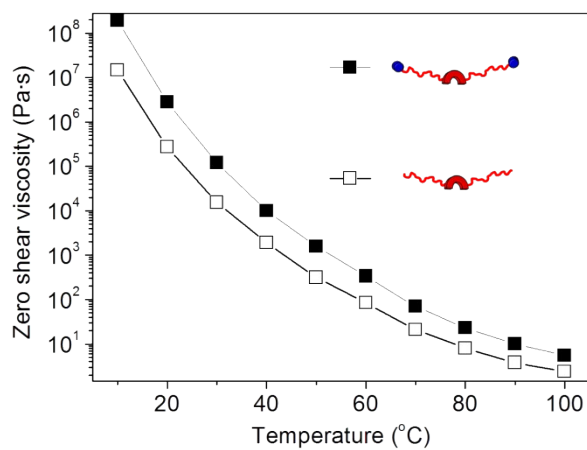
Series	Species	m/z simulated g·mol <sup>-1</sup>	m/z measured g·mol <sup>-1</sup>
①	[H <sub>2</sub> S <sub>4</sub> (C <sub>5</sub> H <sub>5</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>26</sub> C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> + Li <sub>2</sub> - H] <sup>+</sup>	4367.6600	4367.1360
②	[H <sub>2</sub> S <sub>4</sub> (C <sub>5</sub> H <sub>5</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>26</sub> C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> + Li + Na - H] <sup>+</sup>	4383.6337	4383.7083
③	[H <sub>2</sub> S <sub>4</sub> (C <sub>5</sub> H <sub>5</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>26</sub> C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> + Na <sub>2</sub> - H] <sup>+</sup>	4399.6074	4399.3126
④	[H <sub>2</sub> S <sub>4</sub> (C <sub>5</sub> H <sub>5</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>26</sub> C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> + K + Na - H] <sup>+</sup>	4416.5844	4417.0661
⑤	[H <sub>2</sub> S <sub>4</sub> (C <sub>5</sub> H <sub>5</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>27</sub> C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> + Li <sub>2</sub> - H] <sup>+</sup>	4521.7435	4521.1674
⑥	[H <sub>2</sub> S <sub>4</sub> (C <sub>5</sub> H <sub>5</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>27</sub> C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> + Li + Na - H] <sup>+</sup>	4537.6856	4537.7934
⑦	[H <sub>2</sub> S <sub>4</sub> (C <sub>5</sub> H <sub>5</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>27</sub> C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> + Na <sub>2</sub> - H] <sup>+</sup>	4533.6917	4533.3429

**Table S2:** MALDI-TOF MS results of Thy-PTFEA-DAP-PTFEA-Thy.

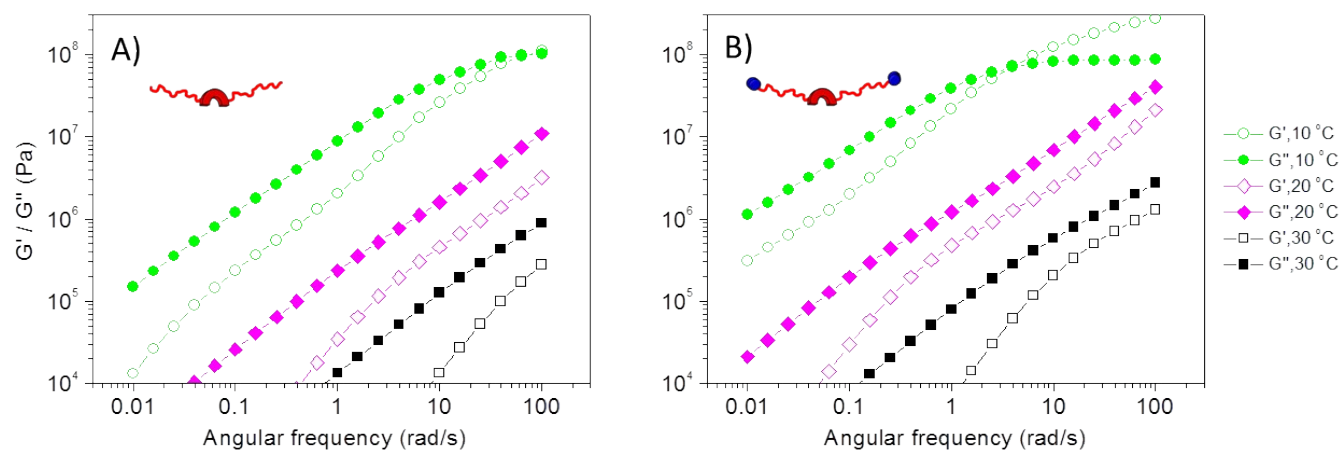
Series	Species	m/z simulated g·mol <sup>-1</sup>	m/z measured g·mol <sup>-1</sup>
①	[(C <sub>9</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> S) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>23</sub> C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> + K <sub>2</sub> + Li + Na <sub>2</sub> - 4H] <sup>+</sup>	4380.3951	4380.9314
②	[(C <sub>9</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> S) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>24</sub> C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> + H] <sup>+</sup>	4403.7797	4403.0365
③	[(C <sub>9</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> S) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>24</sub> C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> + Na <sub>2</sub> - H] <sup>+</sup>	4447.8514	4447.2713
④	[(C <sub>9</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> S) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>24</sub> C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> + K <sub>2</sub> + Li - 2H] <sup>+</sup>	4486.7173	4486.0136
⑤	[(C <sub>9</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> S) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>24</sub> C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> + K <sub>2</sub> + Li + Na <sub>2</sub> - 4H] <sup>+</sup>	4534.8054	4534.3709
⑥	[(C <sub>9</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> S) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>24</sub> C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> + K <sub>2</sub> + Li + Na <sub>3</sub> - 5H] <sup>+</sup>	4556.9246	4556.2481



## Comparative melt rheology

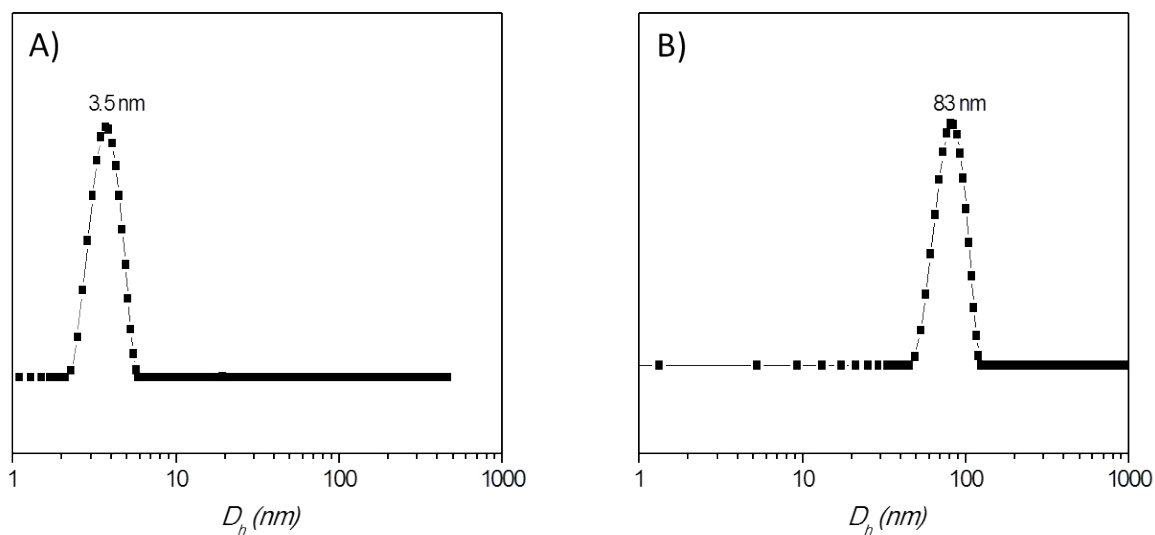


**Figure S4:** Logarithmic plot of the zero shear viscosity vs. temperature of PTFEA-DAP-PTFEA (opened symbols) and Thy-PTFEA-DAP-PTFEA-Thy (closed symbols).



**Figure S5:** Frequency-dependent melt rheology of PTFEA-DAP-PTFEA (A) and Thy-PTFEA-DAP-PTFEA-Thy (B) in the temperature ranging from 10 to 30 °C.

## DLS results of Thy-PTFEA-DAP-PTFEA-Thy



**Figure S6:** DLS results of Thy-PTFEA-DAP-PTFEA-Thy in THF (A) and toluene (B) at 2 g/L.

## References

- [1] S. Chen, A. Bertrand, X. Chang, P. Alcouffe, C. Ladaviere, J.-F. Gerard, F. Lortie, J. Bernard, *Macromolecules*. **2010**, *43*, 5981-5988.
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- [4] a) S. Chen, D. Ströhl, W. H. Binder, *ACS Macro Lett.* **2015**, *4*, 48-52; b) J. Xu, L. Tao, C. Boyer, A. B. Lowe, T. P. Davis, *Macromolecules*. **2010**, *43*, 20-24; c) S. Chen, M. Schulz, B.-D. Lechner, C. Appiah, W. H. Binder, *Polym. Chem.* **2015**, *6*, 7988-7994.