**Supporting Information**

# Supramolecular Polymers with Orthogonal Functionality

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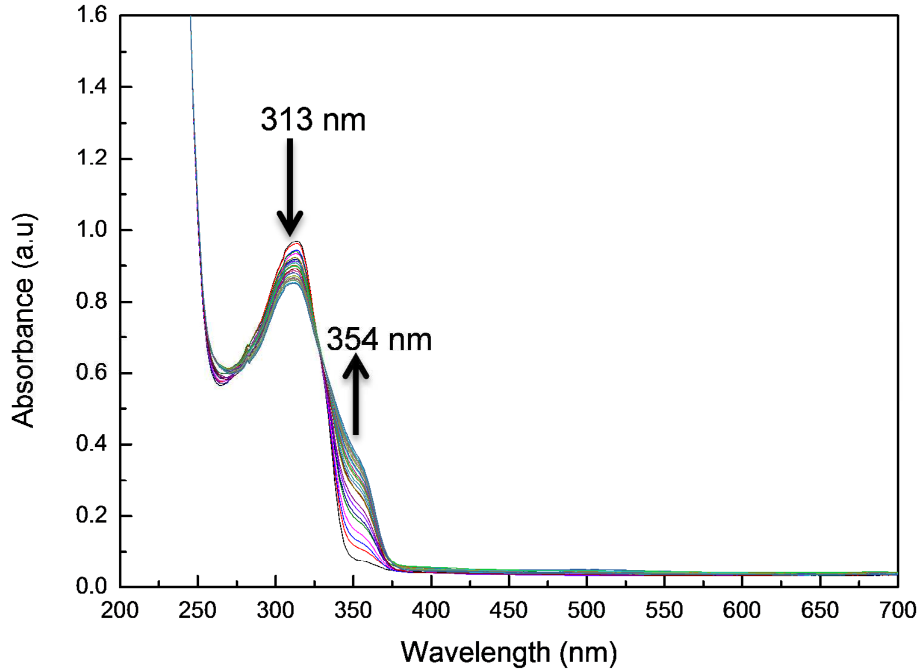


**Figure S1**. UV-Vis spectra acquired upon titration of the neat Mebip-PEB-Mebip with $Zn(NTf_2)_2$. Data were acquired upon adding 25 μL aliquots of a $Zn(NTf_2)_2$ solution in a 9:1 v/v $CHCl_3/CH_3CN$ mixture (416 μM) to a solution of Mebip-PEB-Mebip (18 μM) in the same solvent mixture.

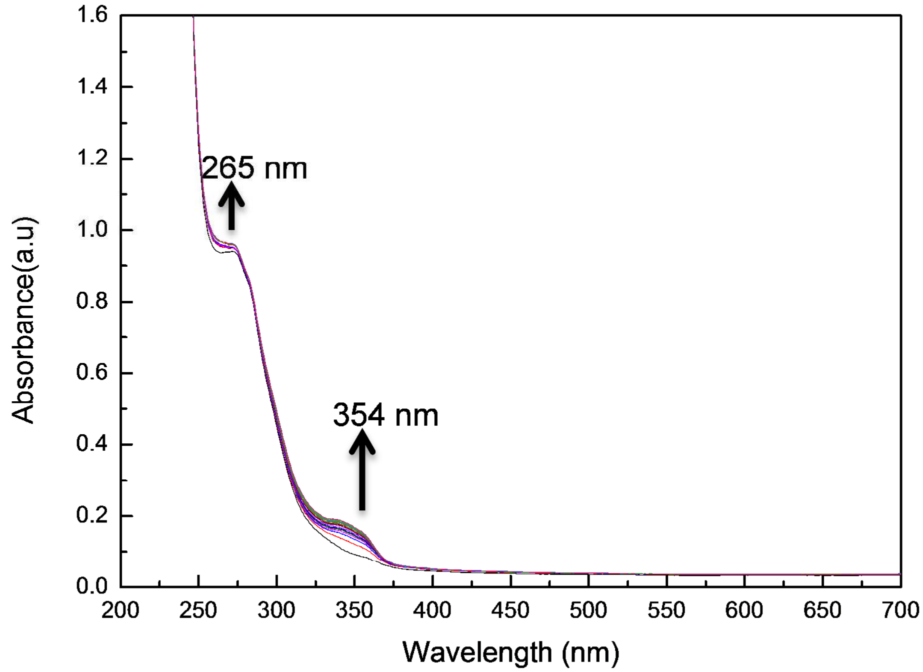


**Figure S2**. UV-Vis spectra acquired upon titration of the neat UPy-PEB-UPy with $Zn(NTf_2)_2$. Data were acquired upon adding 25 μL aliquots of $Zn(NTf_2)_2$ in a 9:1 v/v $CHCl_3/CH_3CN$ mixture (416 μM) to a solution of UPy-PEB-UPy (18 μM) in the same solvent mixture.

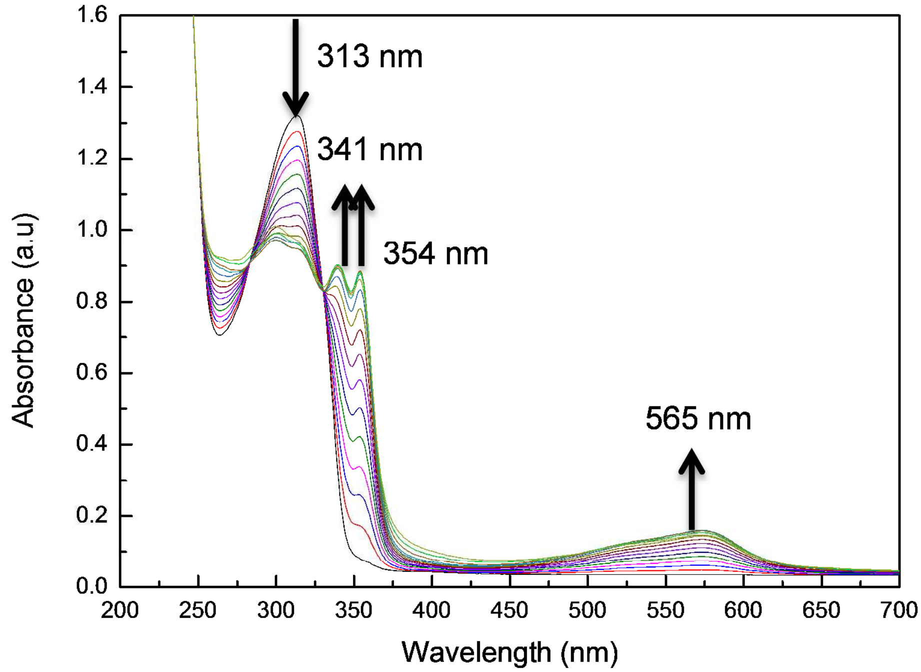


**Figure S3**. UV-Vis spectra acquired upon titration of the neat Mebip-PEB-Mebip with $Fe(ClO_4)_2$. Data were acquired upon adding 25 μL aliquots of a $Fe(ClO_4)_2$ solution in a $CHCl_3/CH_3CN$ (9:1 v/v) mixture to a solution of of Mebip-PEB-Mebip (19 μM) in the same solvent mixture.

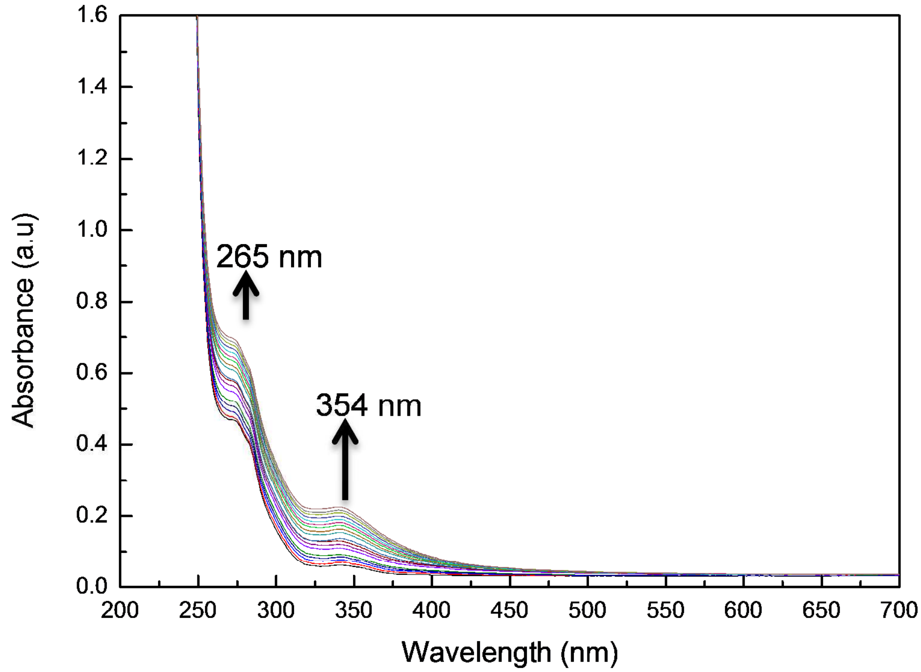


**Figure S4**. UV-Vis spectra acquired upon titration of the neat UPy-PEB-UPy with $Fe(ClO_4)_2$. Data were acquired upon adding verify aliquots of a $Fe(ClO_4)_2$ in a 9:1 v/v $CHCl_3/CH_3CN$ solvent mixture (454 μM) to a solution of UPy-PEB-UPy (19 μM) in the same solvent mixture.

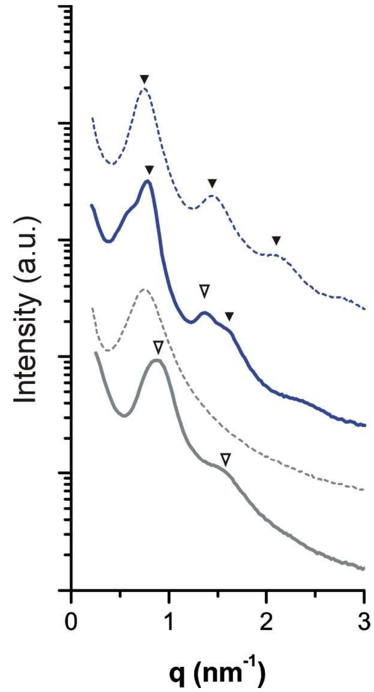


**Figure S5.** SAXS spectra of the blend $\{[Fe(Mebip\text{-}PEB\text{-}Mebip)](ClO_4)_2\}_{1.0}(UPy\text{-}PEB\text{-}UPy)_{1.0}$ acquired one week (—) and two months (- - -) after preparation and of the blend $\{[Fe(Mebip\text{-}PEB\text{-}Mebip)](ClO_4)_2\}_{1.0}(UPy\text{-}PEB\text{-}UPy)_{0.7}$ acquired after one week (—) and two months (- - -) after preparation. The closed and open triangles show the scattering maxima corresponding to lamellar and cylindrical morphologies, respectively. The scattering spectra of the supramolecular polymers blends have been vertically shifted for visualization and clarity.

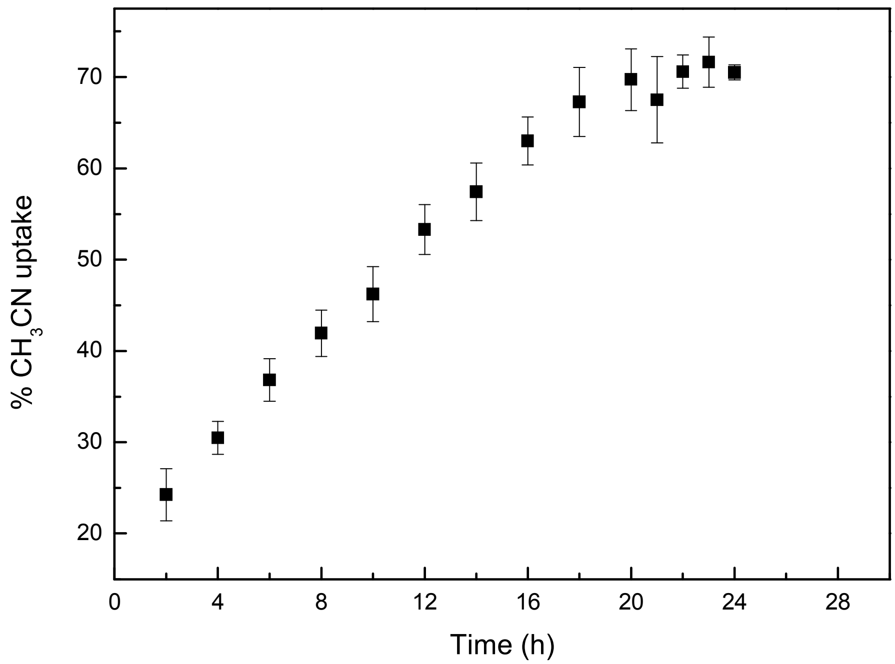


**Figure S6.** Swelling behavior of the blend $\{[Fe(Mebip\text{-}PEB\text{-}Mebip)](ClO_4)_2\}_{1.0}(UPy\text{-}PEB\text{-}UPy)_{0.7.}$ Thin films were placed in $CH_3CN$ at room temperature for the time indicated. The degree of swelling was determined by measuring the weight of the samples pre- and post-swelling. Data points represent averages (number of individual measurements, *n* = 3 ± standard deviation).

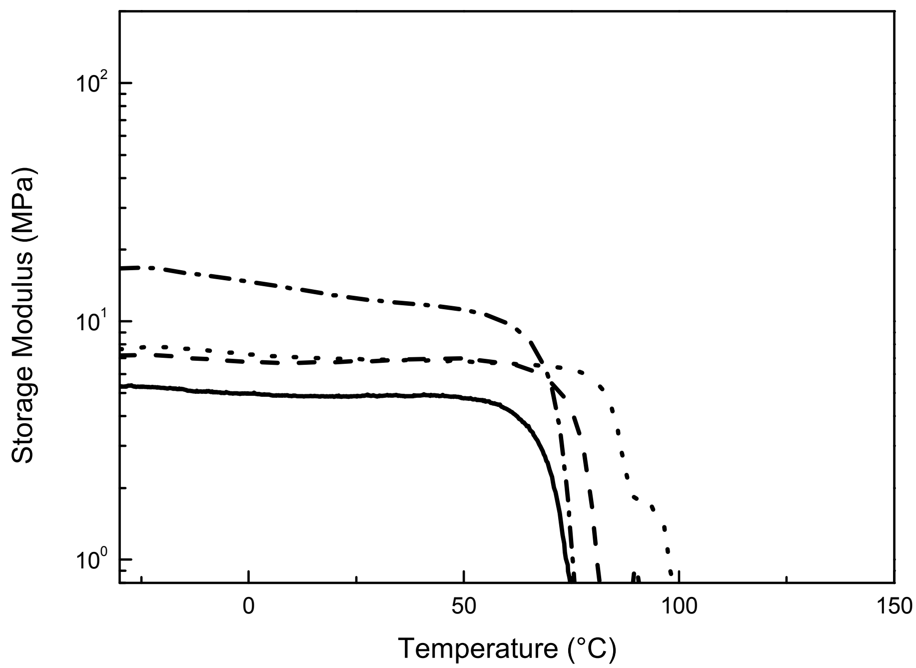


**Figure S7.** Representative dynamic mechanical thermal analysis (DMTA) traces of UPy-PEB-UPy. The neat UPy-PEB-UPy (—) , UPy-PEB-UPy after addition of 40 eq. of PMDETA (vs UPy-PEB-UPy) in $CH_3CN$ solution then swollen for 30 min (---), for 6 h (…) , for 12h (— · —) and subsequently annealed under vacuum for 1 day,.

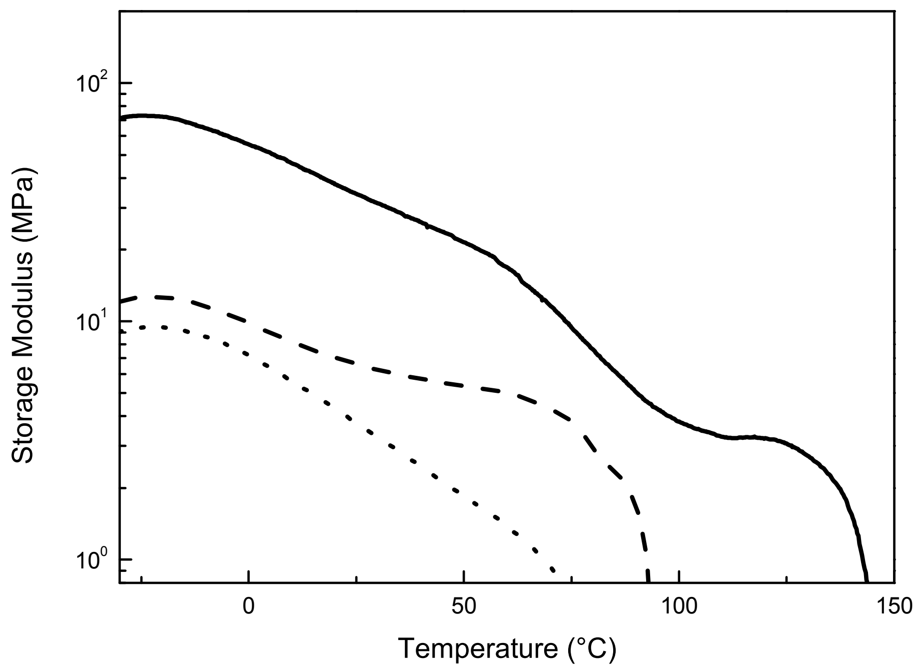


**Figure S8.** Representative dynamic mechanical thermal analysis (DMTA) traces of films [Fe (Mebip-PEB-Mebip)]$(ClO_4)_2$. The neat [Fe(Mebip-PEB-Mebip)]$(ClO_4)_2$ (—) , [Fe (Mebip-PEB-Mebip)]$(ClO_4)_2$ after addition of 40 eq. of PMDETA (vs Mebip-PEB-Mebip) in $CH_3CN$ solution then swollen for 30 min (---), for 6 h (…) and subsequently annealed under vacuum for 1 day.

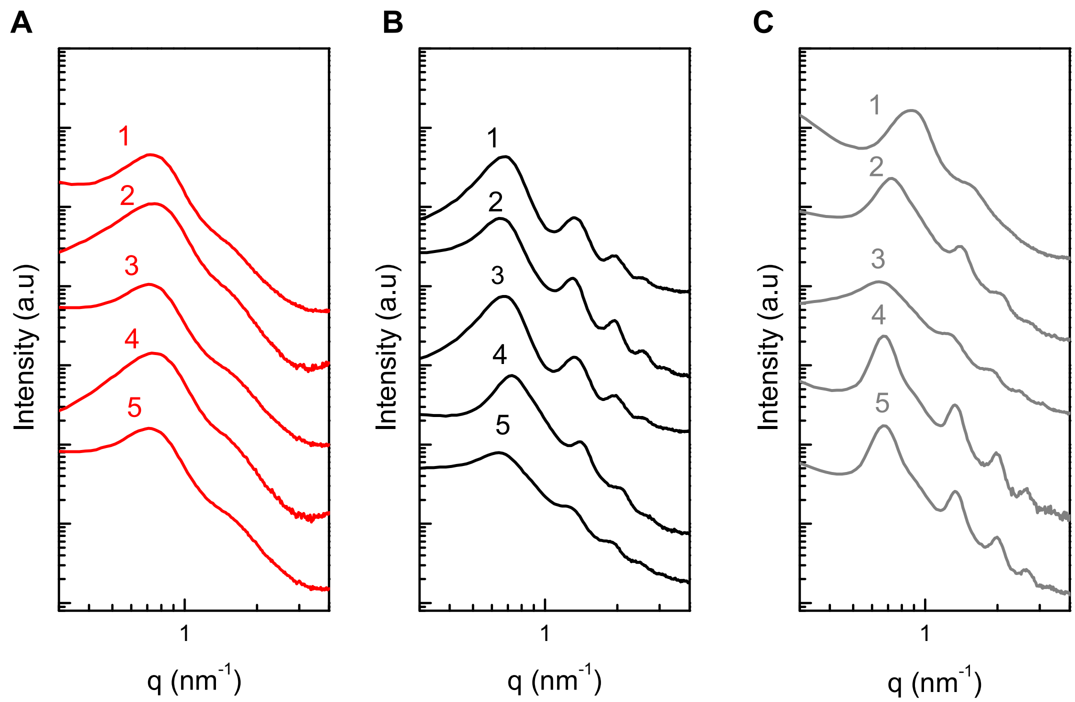


**Figure S9.** SAXS spectra A) for UPy-PEB-UPy (—), B) metallosupramolecular polymer [Fe(Mebip-PEB-Mebip)]$(ClO_4)_2$ (—), C) blends {[Fe(Mebip-PEB-Mebip)]$(ClO_4)_2$}$_{1.0}$(UPy-PEB-UPy)$_{0.7}$ (—) . In all figures 1 corresponds to the neat films, 2 corresponds to films swollen in $CH_3CN$ for 12h and subsequently annealed under vacuum for 1 day. Spectra of 3, 4 and 5 represent the films swollen in $CH_3CN$ with the addition of 40 eq. PMDETA (vs. either UPy-PEB-UPy or Mebip-PEB-Mebip) for 30 min, 6 h, and 12 h, respectively and subsequently annealed under vacuum for 1 day.

**Table S1**. Mechanical properties obtained by stress-strain measurements of supramolecular polymer blends.[a]

| Supramolecular Polymer | Young's Modulus (MPa) | Max. Stress (MPa) | Strain at Break (%) |
|---|---|---|---|
| UPy-PEB-UPy | 9 ± 5 | 1.6 ± 0.7 | 44 ± 6 |
| $[Zn(Mebip\text{-}PEB\text{-}Mebip)](NTf_2)_2$ | 111 ± 13 | 4.6 ± 0.4 | 43 ± 3 |
| $\{[Zn(Mebip\text{-}PEB\text{-}Mebip)](NTf_2)_2\}_{1.0}(UPy\text{-}PEB\text{-}UPy)_{1.0}$ | 21 ± 6 | 2.3 ± 0.1 | 16 ± 4 |
| $\{[Zn(Mebip\text{-}PEB\text{-}Mebip)](NTf_2)_2\}_{1.0}(UPy\text{-}PEB\text{-}UPy)_{0.5}$ | 13 ± 4 | 0.8 ± 0.1 | 12 ± 2 |
| $\{[Zn(Mebip\text{-}PEB\text{-}Mebip)](NTf_2)_2\}_{1.0}(UPy\text{-}PEB\text{-}UPy)_{0.2}$ | 9 ± 3 | 0.3 ± 0.1 | 7 ± 1 |
| $[Fe(Mebip\text{-}PEB\text{-}Mebip)](ClO_4)_2$ | 20 ± 2 | 2.2 ± 0.8 | 33 ± 2 |
| $\{[Fe(Mebip\text{-}PEB\text{-}Mebip)](ClO_4)_2\}_{1.0}(UPy\text{-}PEB\text{-}UPy)_{1.0}$ | 11 ± 3 | 0.9 ± 0.5 | 15 ± 2 |
| $\{[Fe(Mebip\text{-}PEB\text{-}Mebip)](ClO_4)_2\}_{1.0}(UPy\text{-}PEB\text{-}UPy)_{0.7}$ | 10 ± 2 | 0.7 ± 0.1 | 28 ± 1 |
| $\{[Fe(Mebip\text{-}PEB\text{-}Mebip)](ClO_4)_2\}_{1.0}(UPy\text{-}PEB\text{-}UPy)_{0.5}$ | 11 ± 4 | 0.7 ± 0.2 | 31 ± 2 |
| $\{[Fe(Mebip\text{-}PEB\text{-}Mebip)](ClO_4)_2\}_{1.0}(UPy\text{-}PEB\text{-}UPy)_{0.3}$ | 14 ± 3 | 0.8 ± 0.2 | 22 ± 2 |

[a] Data represent averages from three to five samples measured. All samples were measured at 25 °C.

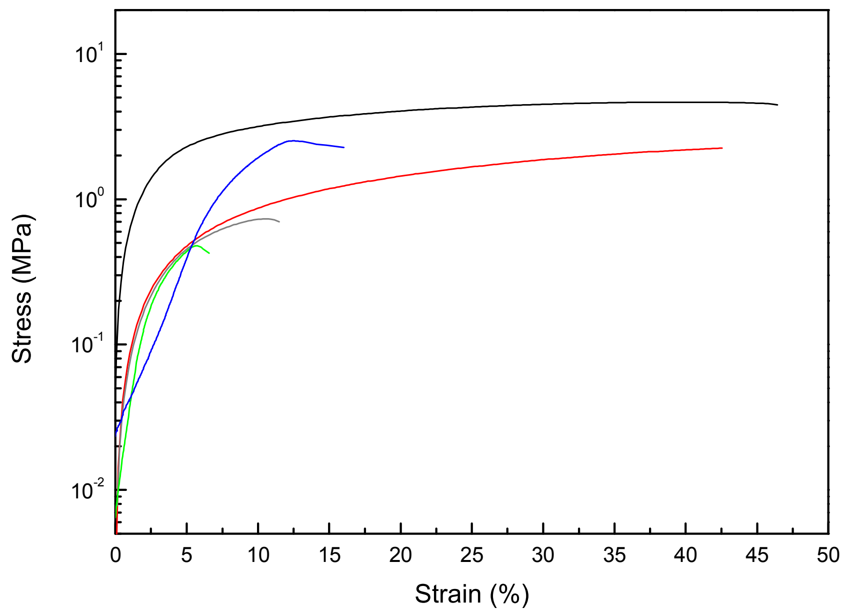


**Figure S10.** Representative stress-strain curves of films of the neat metallosupramolecular polymer [Zn(Mebip-PEB-Mebip)]($NTf_2$)$_2$ (—), the neat UPy-PEB-UPy (—), and the blends {[Zn(Mebip-PEB-Mebip)]($NTf_2$)$_2$}$_{1.0}$(UPy-PEB-UPy)$_{1.0}$ (—), {[Zn(Mebip-PEB-Mebip)]($NTf_2$)$_2$}$_{1.0}$(UPy-PEB-UPy)$_{0.5}$ (—), and {[Zn(Mebip-PEB-Mebip)]($NTf_2$)$_2$}$_{1.0}$(UPy-PEB-UPy)$_{0.2}$ (—). Shown are the data acquired at 25 °C.

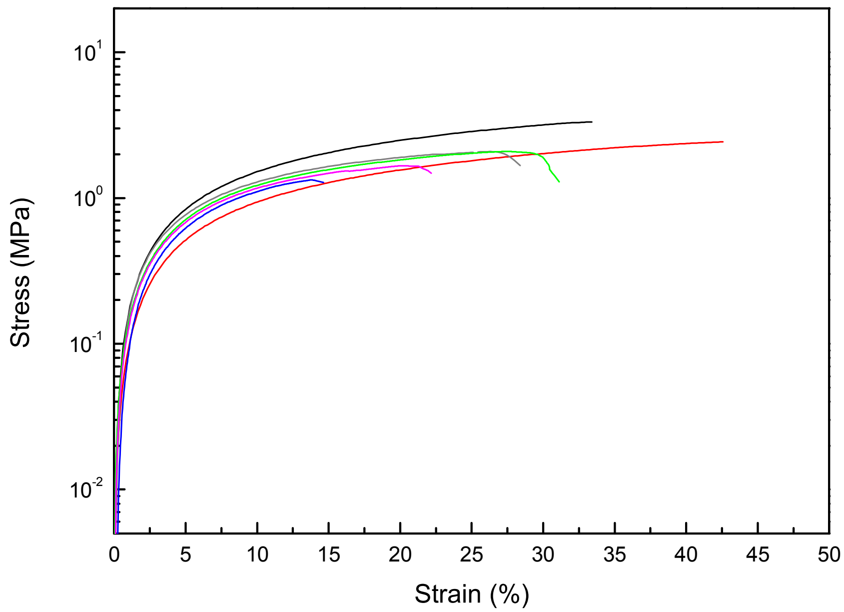


**Figure S11.** Representative stress-strain curves of films of the neat metallosupramolecular polymer [Fe(Mebip-PEB-Mebip)]$(ClO_4)_2$ (—), the neat UPy-PEB-UPy (—), and the following blends $\{$[Fe(Mebip-PEB-Mebip)]$(ClO_4)_2\}_{1.0}$(UPy-PEB-UPy)$_{1.0}$ (—),$\{$[Fe(Mebip-PEB-Mebip)]$(ClO_4)_2\}_{1.0}$(UPy-PEB-UPy)$_{0.7}$ (—), $\{$[Fe(Mebip-PEB-Mebip)]$(ClO_4)_2\}_{1.0}$(UPy-PEB-UPy)$_{0.5}$ (—), and $\{$[Fe(Mebip-PEB-Mebip)]$(ClO_4)_2\}_{1.0}$(UPy-PEB-UPy)$_{0.3}$ (—). Shown are the data acquired at 25 °C.

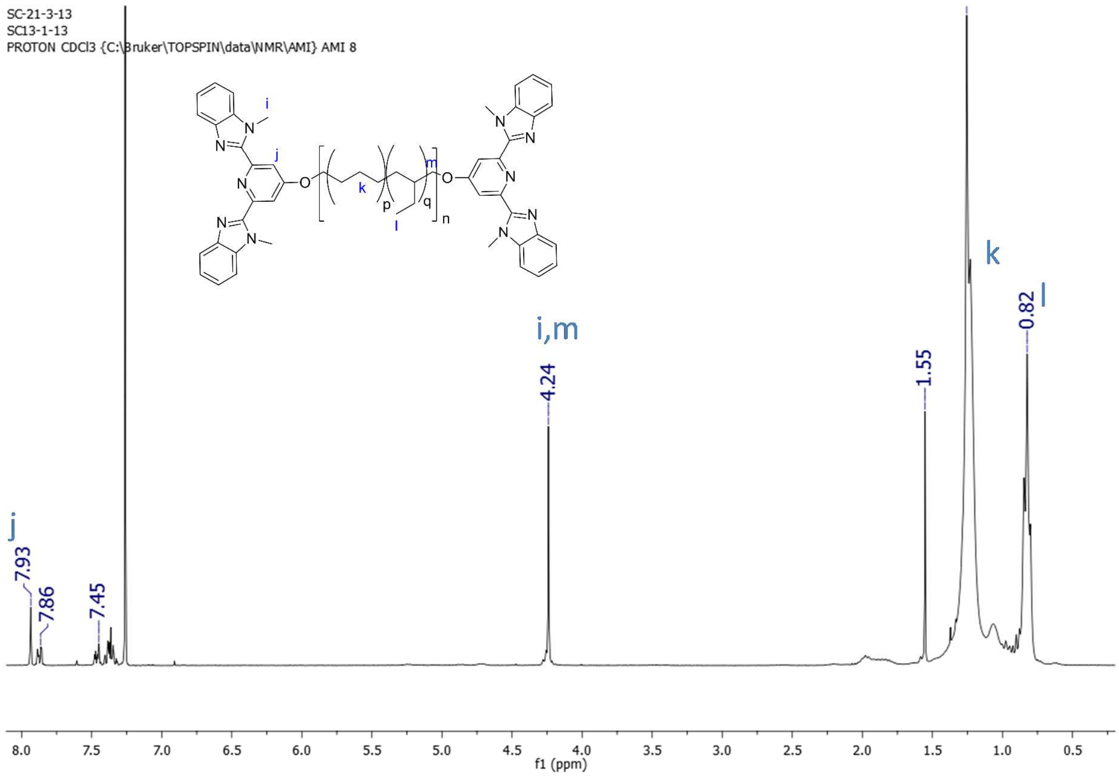


**Figure S12.** $^1$H NMR spectra of Mebip-PEB-Mebip.

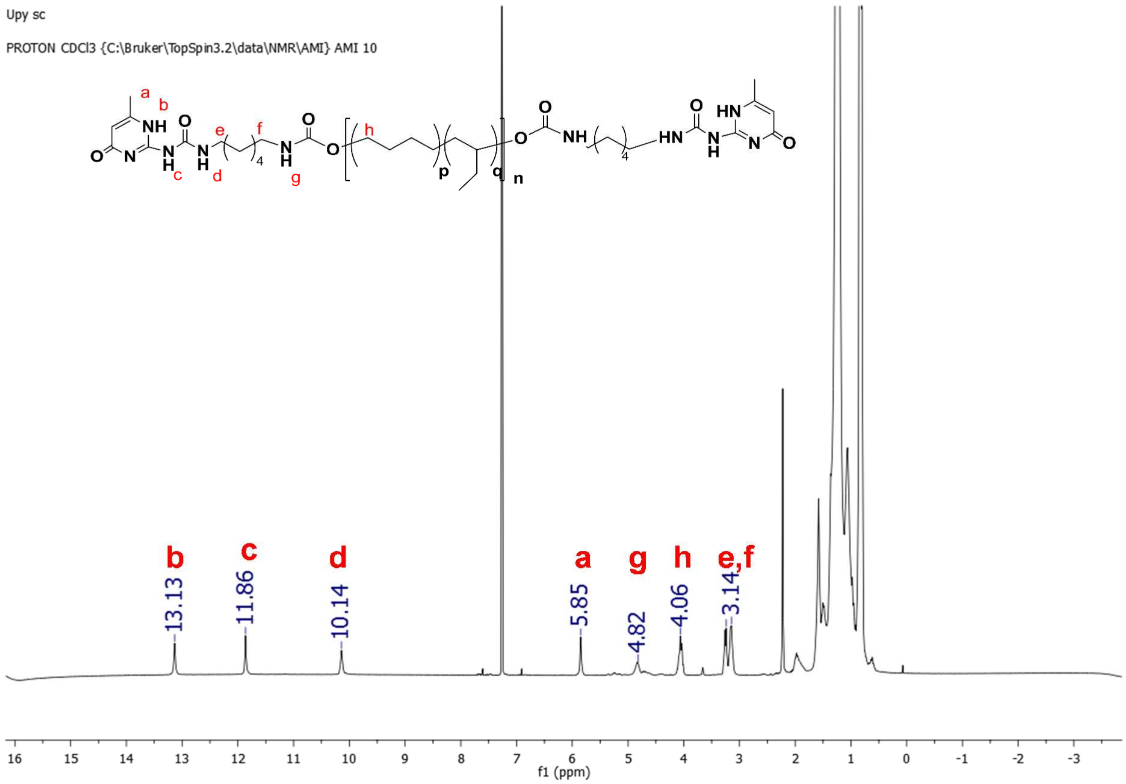


**Figure S13.** $^{1}$H NMR spectra of UPy-PEB-UPy.

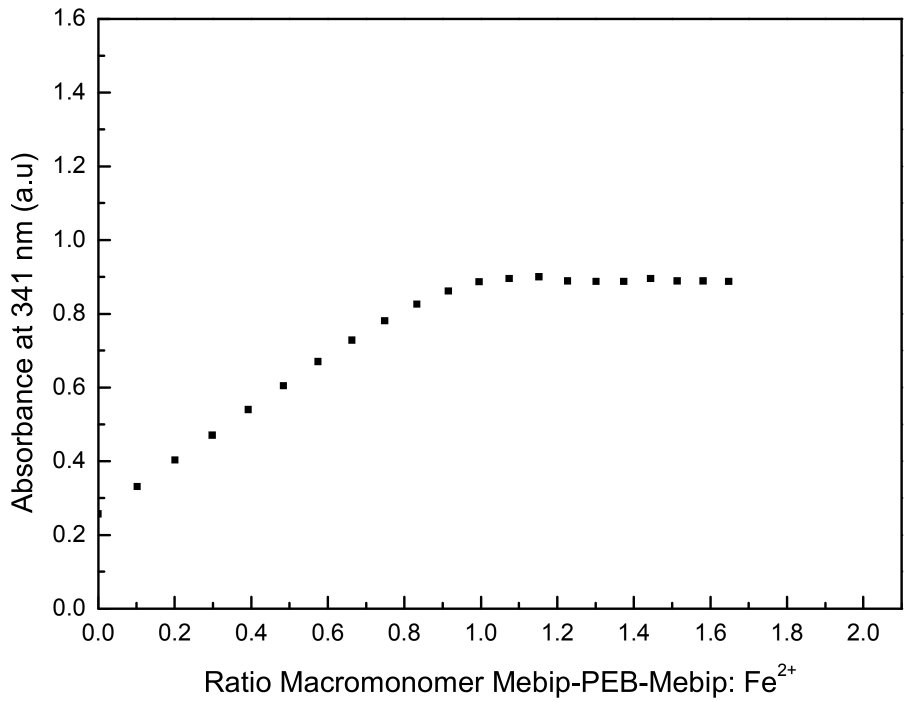


**Figure S14.** Titration of the macromonomer Mebip-PEB-Mebip with $Fe(ClO_4)_2$. Data were acquired upon adding 25 μL aliquots of a $Fe(ClO_4)_2$ solution in a 9:1 v/v $CHCl_3$:$CH_3CN$ mixture to Mebip-PEB-Mebip (25 μM) in the same solvent. Absorption at 354 nm was recorded as a function of the $Fe^{2+}$: Mebip-PEB-Mebip ratio, and the 1:1 ratio suggests full end-capping of the Mebip-PEB-Mebip macromonomer.