Electronic Supplementary Material (ESI) for Biomaterials Science.

# SUPPORTING INFORMATION

# Multi-component supramolecular fibers with elastomeric properties and controlled drug release

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## General materials and instrumentations

All solvents and chemicals were purchased from Sigma-Aldrich or Carlo Erba and used without further purification. 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) was purchased from Fluorochem (UK).

Reversed phase high pressure liquid chromatography–mass spectrometry (RP-HPLC-MS) was performed on a system with an Alltima C18 3u (50 mm x 2.1 mm) reversed phase column and gradients of acetonitrile in water (supplemented with 0.1% formic acid). $^{1}$H-NMR and $^{13}$C-NMR spectra were recorded on a 400 MHz NMR (Varian Mercury Vx or Varian 400MR) operating at 400 MHz for $^{1}$H-NMR and 100 MHz for $^{13}$C-NMR. Proton chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) and carbon chemical shifts in ppm downfield from TMS using the resonance of the deuterated solvent as internal standard. Abbreviations used are s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. Differential Scanning Calorimetry (DSC) spectra were obtained on a TA-instruments DSC Q2000 with heating and cooling rates of 10 °C/min during first and second heating runs. Gel Permeation Chromatography (GPC) was carried out in analytical grade dimethylformamide (DMF) with an integrated HPLC–detection system PL-GPC 50 Plus from Polymer Laboratories (a Varian company). The instrument houses a refractive index detector and operates with DMF with 10 mM LiBr mobile phase at 1.0 mL/min flow rate. Calibration of this GPC system was done with poly(ethylene oxide) (PEO) standards from Polymer Standard Service, Inc. (Warwick, USA).

## Supplementary Data

**Table 1.** Bulk properties of chain-extended UPy-PEG hydrogels, in comparison with the elastomeric component chain-extended UPy-PC.

| Polymer | Soft block length [g $mol^{-1}$] | $M_n$ [a)] [kg $mol^{-1}$] | $M_w$ [a)] [kg $mol^{-1}$] | $T_g$ [b)] [°C] | $T_m$ [b)] [°C]a | $\Delta H_m$ [b)] [J $g^{-1}$] |
|---|---|---|---|---|---|---|
| UPy-PC | 1000 | 19.4 | 47.7 | -33 | 123 | 1.6 |
| UPy-$PEG_{600}$ | 600 | 15.4 | 30.0 | -48 | 66/112 | 7.9/11.5 |
| UPy-$PEG_{1000}$ | 1000 | 20.6 | 61.7 | -47 | 63/102 | 5.4/8.5 |
| UPy-$PEG_{1500}$ | 1500 | 14.4 | 29.9 | -54 | 67/110 | 5.0/7.0 |

[a)] Average molecular weight determined by gel permeation chromatograpy (GPC) in DMF/LiBr based on poly(ethylene oxide) (PEO) standards; [b)] Thermal data refer to the second heating run of differential scanning calorimetry (DSC) experiments at 10°C/min on the dry polymers.

**Table S2**. Bulk tensile properties of chain-extended UPy-PEG hydrogels, in comparison with the elastomeric component chain-extended UPy-PC (E: Young's modulus, $\varepsilon_{max}$: elongation at break, UTS: ultimate tensile strength). Data are expressed as average ± standard deviation.

| **Polymer** | **E dry [MPa]** | **E wet [MPa]** | **UTS dry [MPa]** | **UTS wet [MPa]** | **$\varepsilon_{max}$ dry [%]** | **$\varepsilon_{max}$ wet [%]** |
|---|---|---|---|---|---|---|
| UPy-PC | 8 ± 1 | - | 71 ± 6 | - | 614 ± 20 | - |
| UPy-$PEG_{600}$ | 99 ± 11 | 40 ± 2 | 22 ± 1 | 18 ± 9 | 425 ± 11 | 382 ± 133 |
| UPy-$PEG_{1000}$ | 16 ± 2 | 19 ± 8 | 9 ± 1 | 9 ± 5 | 533 ± 33 | 363 ± 177 |
| UPy-$PEG_{1500}$ | 27 ± 9 | 13 ± 3 | 14 ± 4 | 6 ± 2 | 480 ± 90 | 230 ± 102 |

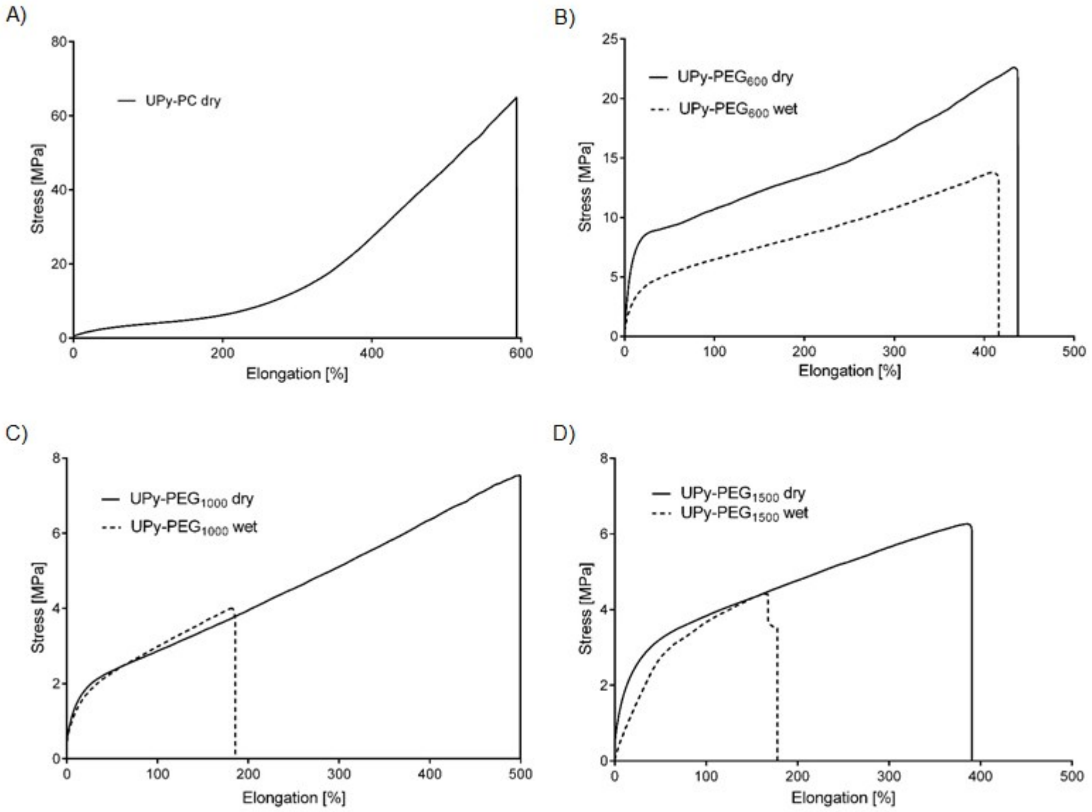


**Figure S1. Bulk tensile properties of polymers used in this study.** Representative tensile curves of polymers used in this study. A) UPy-PC; B) UPy-PEG$_{600}$ in dry (solid line) and wet (dashed line) conditions; C) UPy-PEG$_{1000}$ in dry (solid line) and wet (dashed line) conditions; D) UPy-PEG$_{1500}$ in dry (solid line) and wet (dashed line) conditions.

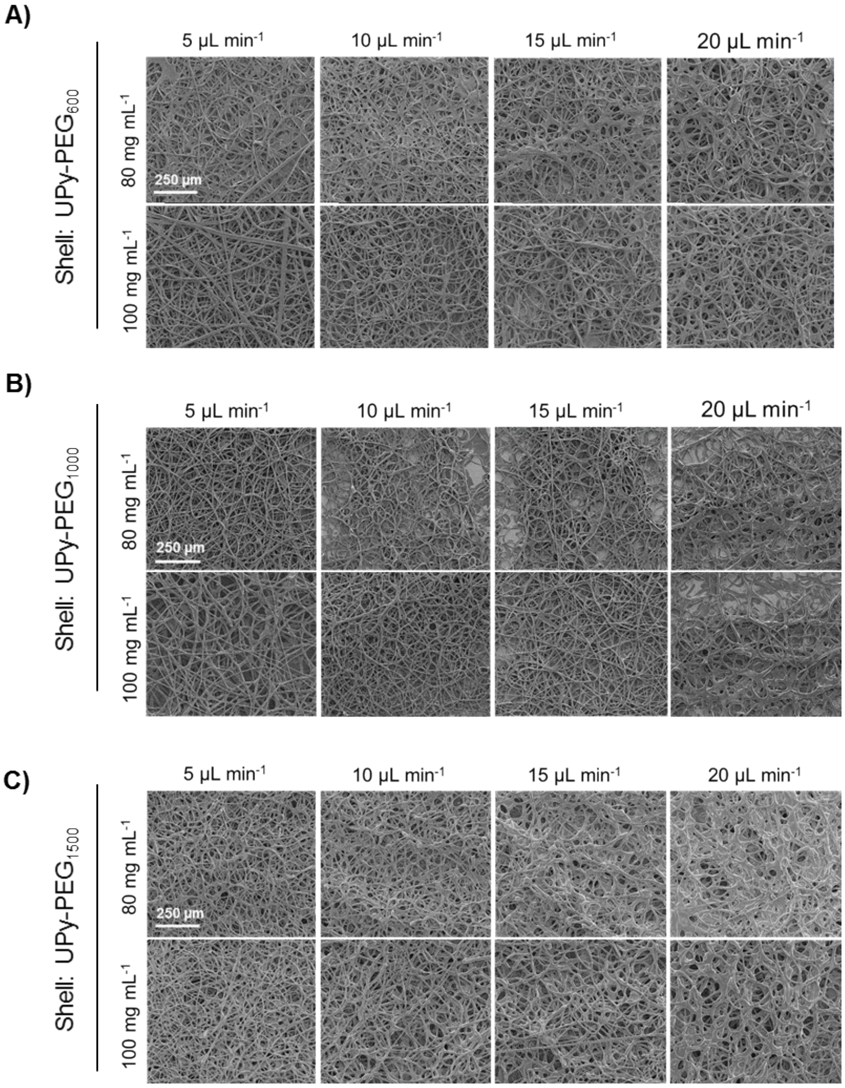
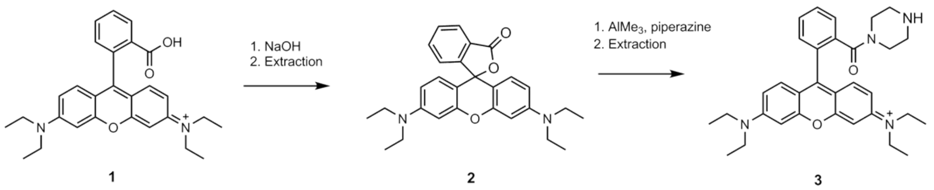


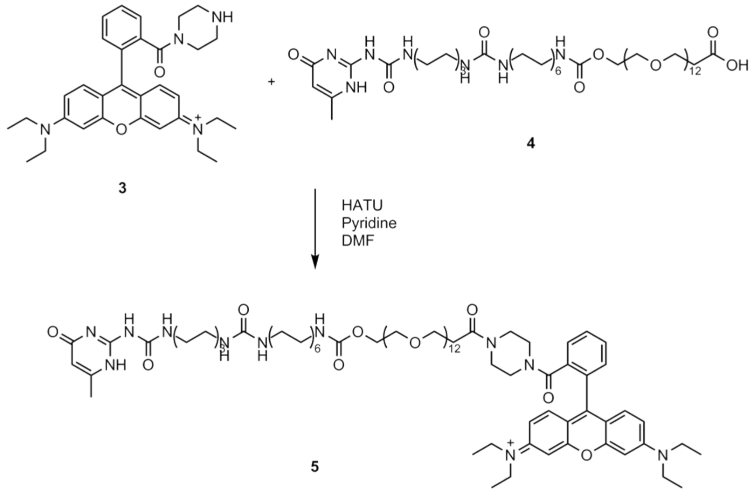
**Figure S2. Morphology of fibers fabricated by coaxial electrospinning.** SEM micrographs of core-shell fibers fabricated with a UPy-PC core solution with constant flow and concentration, and a shell UPy-PEG solution containing UPy-PEG$_{600}$ (A), UPy-PEG$_{1000}$ (B) or UPy-PEG$_{1500}$ (C). The flow rate and concentration of the shell solution were varied between 5 and 20 µL min$^{-1}$ and 80 and 100 mg mL$^{-1}$. Scale bars represent 250 µm.

**Table S3**. Thermal properties (thermal and processing history-derived; 1st heating run of DSC experiments. Heating from 20°C to 160°C at 10°C/min) of electrospun core-shell meshes and bulk single components.

| | $T_m$ [°C] | $\Delta H_m$ [J g$^{-1}$] |
|---|---|---|
| **Electrospun mesh (1st heating run)** | | |
| UPy-PC | 58/93 | 4.3/1.9 |
| UPy-PC / UPy-PEG$_{600}$ | 69/125 | 2.2/3.6 |
| UPy-PC / UPy-PEG$_{1000}$ | 81/126 | 5.8/1.0 |
| UPy-PC / UPy-PEG$_{1500}$ | 40/78/124 | 0.6/5.0/0.4 |
| **Bulk (1st heating run)** | | |
| UPy-PC | 66/125 | 0.8/0.2 |
| UPy-PEG$_{600}$ | 76/116 | 9.5/9.4 |
| UPy-PEG$_{1000}$ | 71/123 | 4.1/5.5 |
| UPy-PEG$_{1500}$ | 46/85/117 | 2.2/2.1/2.8 |



**Scheme S1**. Synthesis of Rhodamine B piperazine amide (RohdBP) (**3**)



**Scheme S2**. Synthesis of UPy-conjugated Rhodamine B piperazine amide (UPy-RohdBP) (**5**)

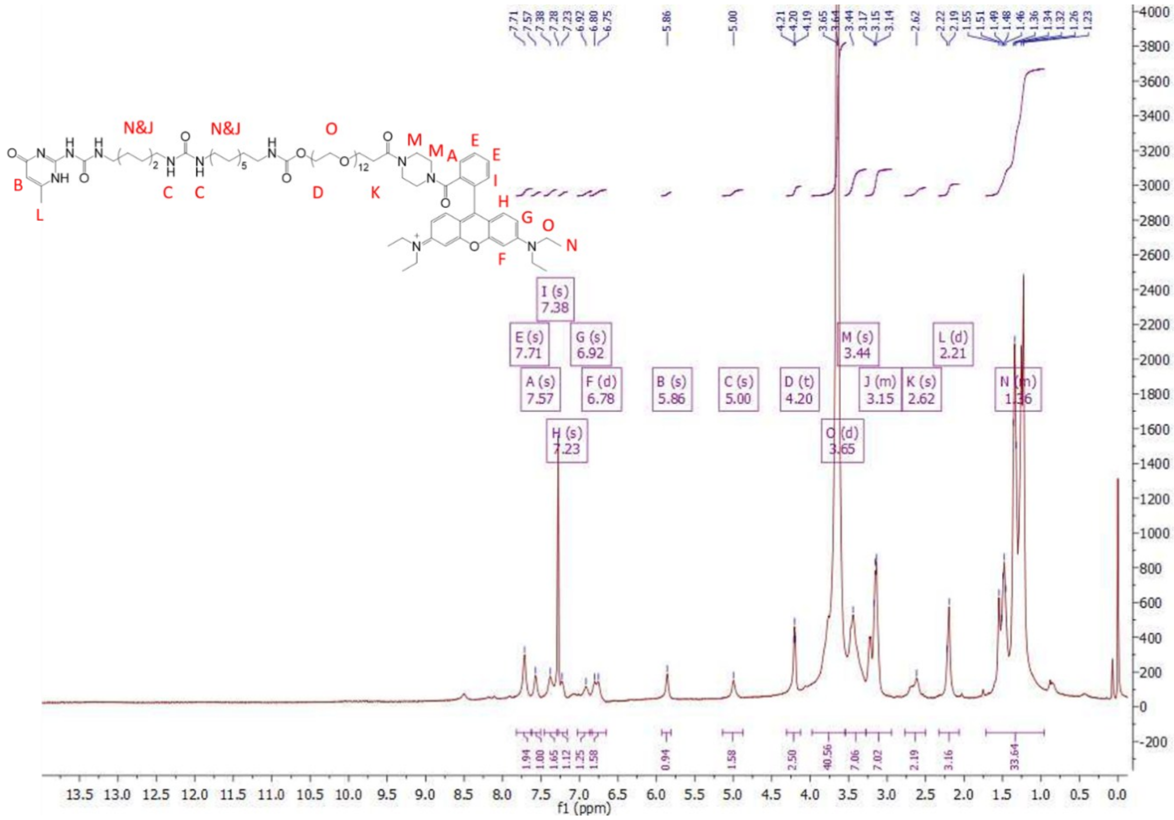


**Figure S3.** $^1$H-NMR (400 MHz) of UPy-RohdBP.