Electronic supplementary information

Dual-compartment nanofibres: Separation of two highly reactive components in close vicinity

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Instruments and Characterization

Column chromatography was performed on silica gel (Geduran Si60, Merck). ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX 250 and Bruker Avance 300 spectrometers. FD mass spectra were measured with a VG-instruments ZAB 2-SE-FPD instrument. UV/Vis spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer. Fluorescence spectra were recorded on a Spex Fluorolog 3 spectrometer. FT-IR spectroscopy measurements were carried out on a Bruker ALPHA FT-IR spectrometer equipped with an ATR diamond, a SiC light source and a DTGS detector at RT. DSC measurements were carried out on a Netzsch 204 F1 Phoenix differential scanning calorimeter with heating rates of 10 Kmin^{-1} under N$_2$ atmosphere in a temperature range from 0 to 180 °C. 5-15 mg samples were used for the measurements. To monitor the curing for the bulk references the epoxy was first mixed with the PVA and the cooled amine was balanced into the crucible lid and both components were pressed together immediately before the measurement. HPLC measurements were performed on a Macherey Nagel Pyramid column (Dimensions: 125/4 mm/ 5 µmm) with CHCl$_3$/CH$_3$OH (95/5) as eluent with a flow rate of 1 mLmin^{-1} at 20 °C and a UV-Detector at a detection wavelength of $\lambda = 276$ nm.
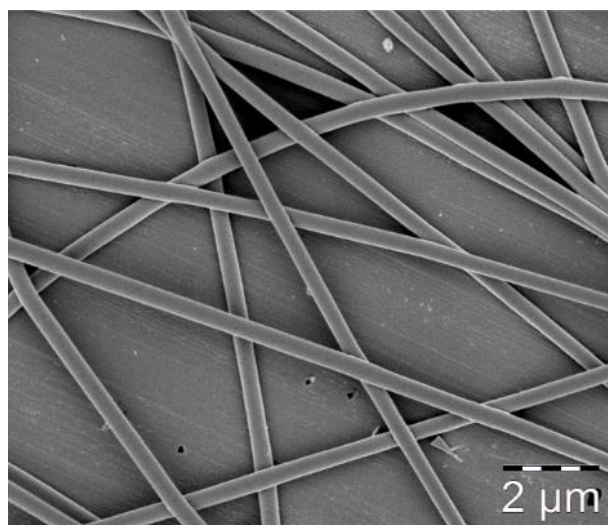

**Figure S1.** SEM image of the pure PVA fibres as reference.

Table S1. Summary of the colloidal properties of the emulsions, details regarding the fibres and their epoxy-amine loads. From the calculations a number ratio of amine nanoparticles to epoxy nanoparticles of ca. 1.91/1 can be deduced.

Entry	Mean diameter [nm] (PDI)	droplet number/g EA dispersion[a]	Ratio PVA/ EA	C_{PVA} [wt.%]	Mean fibre diameter[b] [nm]
Amine Me	137 (0.093)	$4.4*10^{15}$			
Epoxy Me	153 (0.099)	$2.3*10^{15}$			
PVA control			-	10	361 ± 14
PVA-EA 0			6:1	12	319 ± 54
PVA-EA			3:1	10	311 ± 50
PVA-EA 2			2:1	8.6	165 ± 18
PVA-EA 3			1:1	5	73 ± 31

[a] Calculated on basis of the DLS data (with $\rho_{epoxy} = 1.16$ g/cm³; $\rho_{amine} = 0.979$ g/cm³ (measured with a pygnometer); AHEW = 220 g/eq., EEW = 187 g/ eq.). [b] Calculated via SEM. The viscosity (25 °C) of the amine was 1530 mPas and of the epoxide about 12 000 mPas.

Synthesis of 3,9(10)-bis(4-*tert*-butylphenyl)perylene
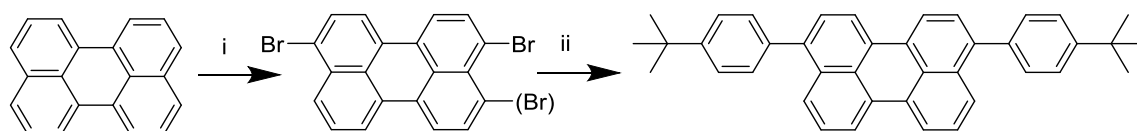
Scheme S1. *i*, Br$_2$, AcOH; *ii,* 4-*tert*-butylphenyl boronic acid, Pd(PPh$_3$)$_4$, K$_2$CO$_3$ aq, toluene.

3,9(10)-Dibromoperylene was synthesized by bromination of perylene as described before.[1]

3,9(10)-Bis(4-*tert*-butylphenyl)perylene. 3,9(10)-dibromoperylene (410 mg, 1 mmol) and 4-*tert*-butylphenyl boronic acid (534 mg, 3 mmol) were dissolved in the mixture of toluene (40 ml) and ethanol (5 ml) in 100 ml Schlenk flask and flushed with argon. After stirring at 80 °C for 20 min Pd(PPh$_3$)$_4$ (100 mg) and aqueous 2M K$_2$CO$_3$ (5 ml) were added to the solution. The reaction mixture was stirred at 90 °C for 12 h under argon. After cooling the resulting mixture was washed with water and extracted with toluene. The combined organic extracts were evaporated *in vacuo* and purified by column chromatography on silica gel using petrol ether: dichloromethane, 3:1 as eluent. Yield 400 mg (77.5%). **^{1}H-NMR (250 MHz, CD$_2$Cl$_2$, 25 °C):** δ = 8.15-8.20 (m, 4H), 7.79 (d, ^3J=8.44 Hz, 2H), 8.36-7.48 (m, 12H), 1.35 (s, 18H) ppm; **^{13}C-NMR (75 MHz, C$_2$D$_2$Cl$_4$, 25 °C):** δ= 150.59, 140.25, 140.16, 137.64, 133.14, 131.74, 131.58, 130.70, 130.54, 129.88, 129.14, 128.19, 126.89, 125.63, 120.84, 120.60, 120.51, 120.27, 34.86, 31.76 ppm; UV-vis (toluene) λ$_{max}$: 460 (ε/ dm^3 mol^{-1} cm^{-1} 48000), 433 (38900) nm. Fluorescence (toluene): 482 nm (ϕ=97%). MS (FD): [M+], calculated for C$_{40}$H$_{36}$, 516.73; found, 517.1 (100%), M+.
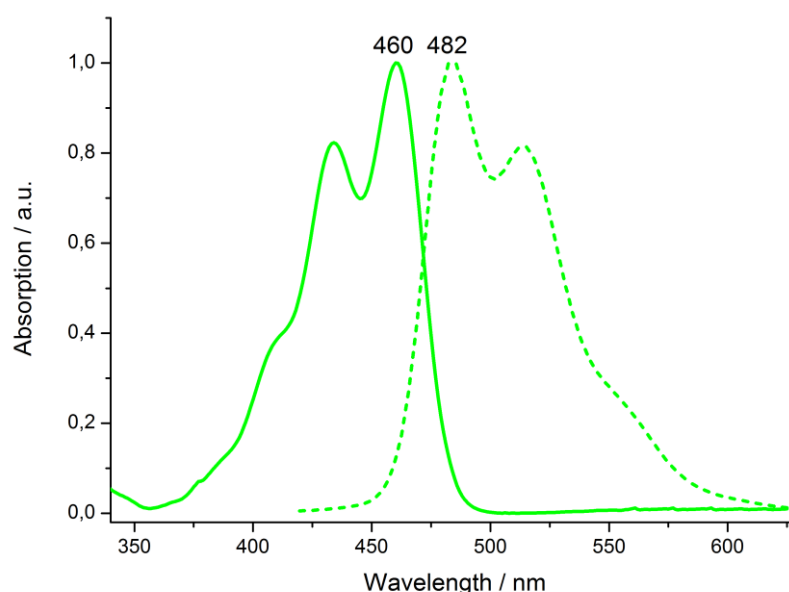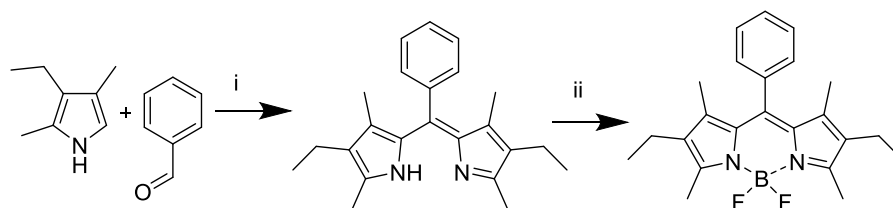

Figure S2. Absorption and emission spectra of diphenylperylene in toluene.

Synthesis of BODIPY (2,6-Diethyl-1,3,5,7-tetramethyl-8-phenyl-4,4'-difluoroboradiaza-indacene)

Scheme S2. i, TFA, dichloromethane, DDQ; ii, BF$_3$ etherate, Et$_3$N, dichloromethane.

The two-step synthesis was performed according to the literature.[2]
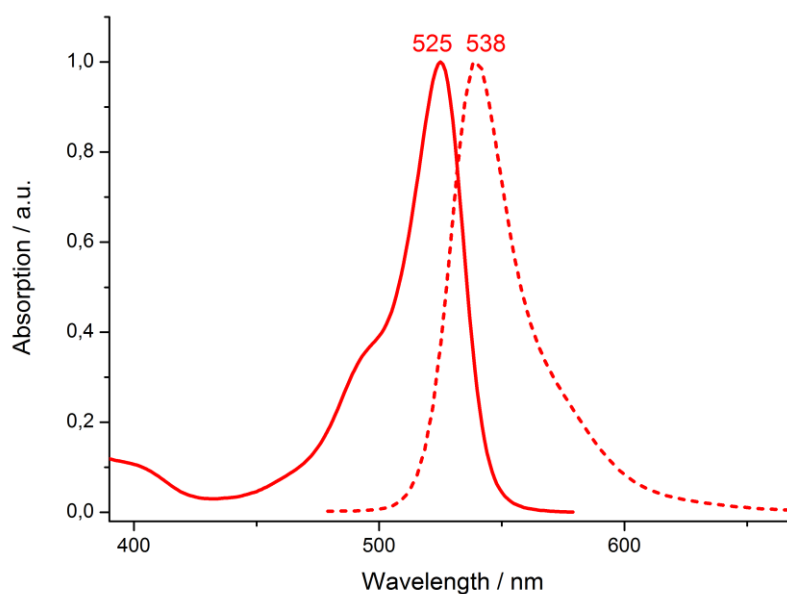

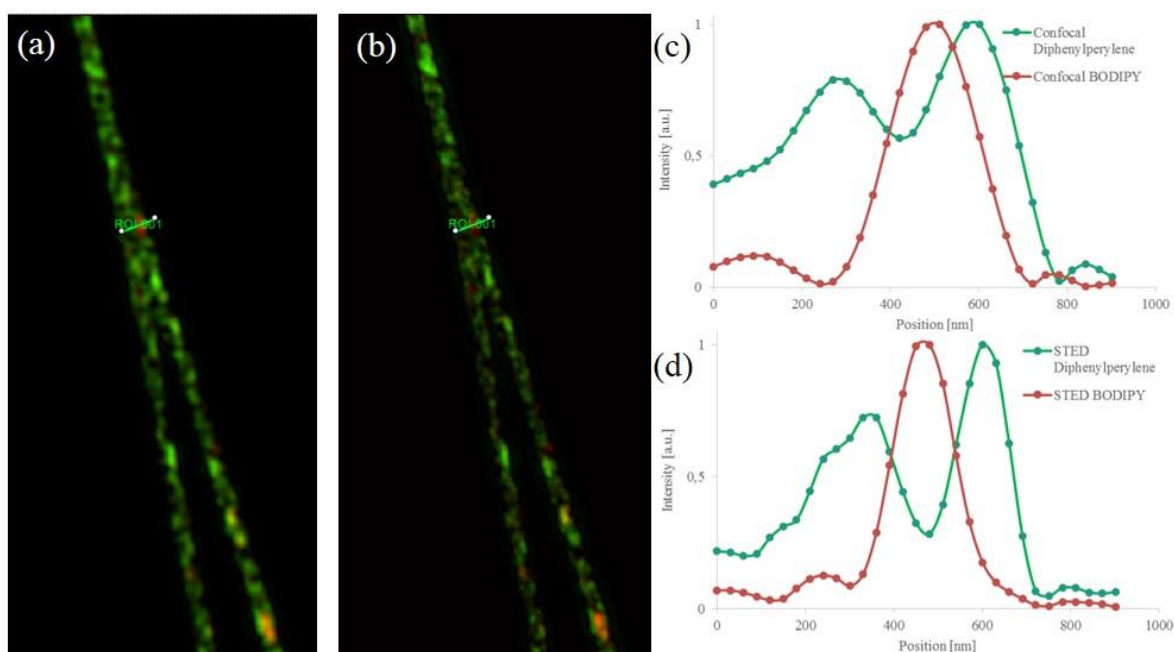**Figure S3.** Absorption and emission spectra of BODIPY in toluene.

Figure S4. Comparison of a) confocal image versus b) STED image. The graphs show the intensity for both colour channels along the line profile shown in both images for the c) confocal image and d) for the STED image.

Figure S4 shows the advantage of STED versus confocal imaging. For this comparison, a section of Figure 3a) was enlarged (Figure S4b) and compared to the same section in confocal imaging (S4a). For confocal deconvolution the same algorithm/parameters were used as for the STED image, except for the PSF, assuming a Gaussian distribution of 230 nm. In Figure S4c-d) the intensity profiles along the lines marked in Figure S4a) and b) are depicted for the diphenylperylene and BODIPY channel. It is obvious, that the usage of STED allows for a better separation and resolution of the compartments. Full width half maximum (FWHM) of the BODIPY compartment is ~230 nm in confocal mode as compared to 170 nm using STED imaging. For the diphenylperylene compartment, STED shows FWHM of ~130 nm as compared to ~230 nm in the confocal mode.

Reactivity of the PVA-EA nanofibres

Since the crosslinking of the epoxy with the amine is an exothermic process, we performed DSC measurements on the dual-compartment nanofibres. All PVA containing samples show a broad endothermic signal at about 60 °C originating from adsorbed or entrapped water and was found to be more distinct for the nanofibres.[3] In Figure S5 a) we plotted the enthalpy changes for the pure epoxy-amine curing (red) with ternary mixtures of the epoxy-amine plus PVA. The reaction appears as a broad peak which is difficult to see in DSC. By artificially increasing the PVA to EA ratio we were able to verify the results. The enthalpy change per gram of epoxide is given in Table S2.
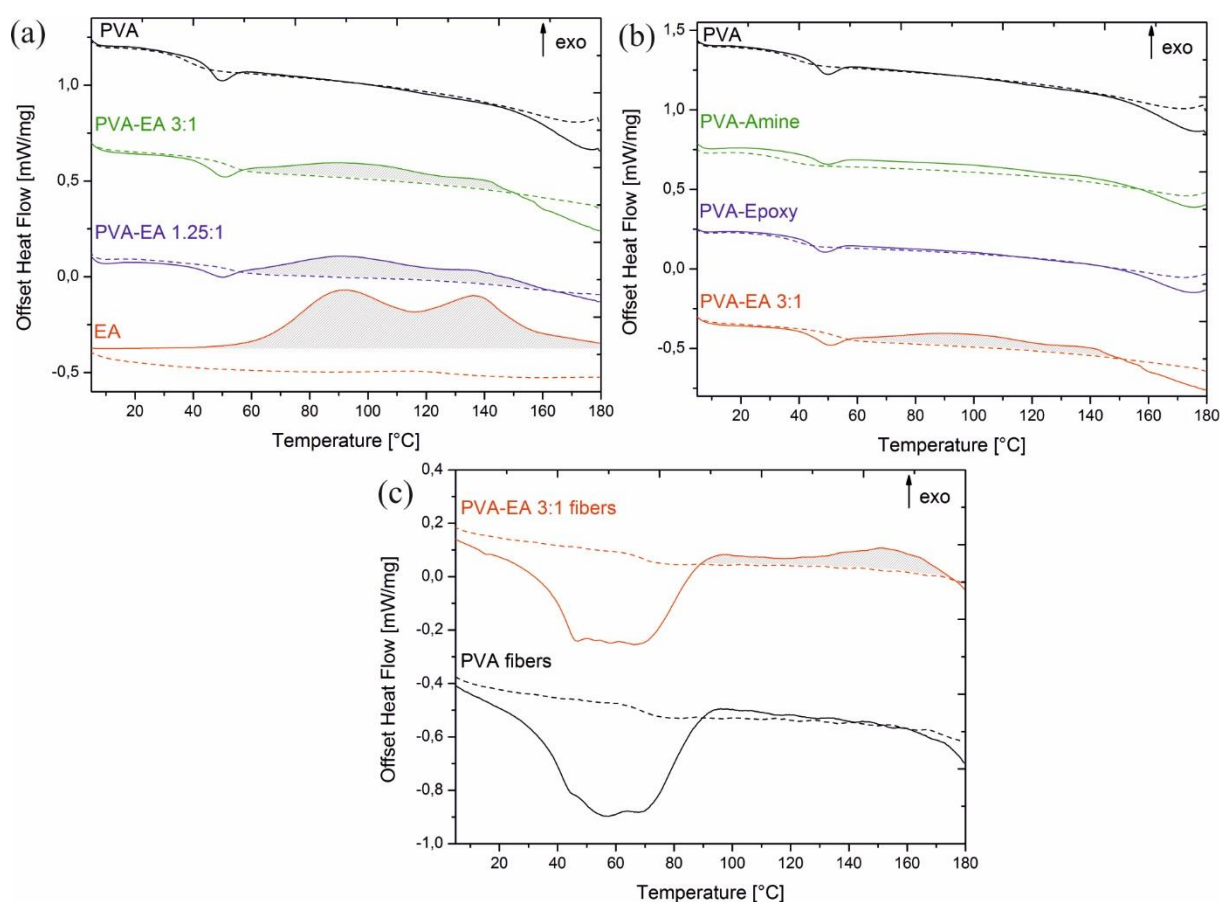

Figure S5. DSC curves of the epoxy-amine curing as bulk references. 2nd heating cycles are depicted as dashed lines. a) Black: pure PVA powder; green: PVA powder mixed with epoxy and amine (ratio 3:1); blue: artificially increased ratio of 1.25:1; red: pure curing reaction. b) Mixtures of PVA powder with the individual components to ensure that the measured enthalpy origins from the curing reaction only. c) Comparison of the pure PVA fibres (black) and the PVA-EA fibres (red).

Table S2. Reaction enthalpies of the curing reaction as Joules per gram epoxide for comparison.

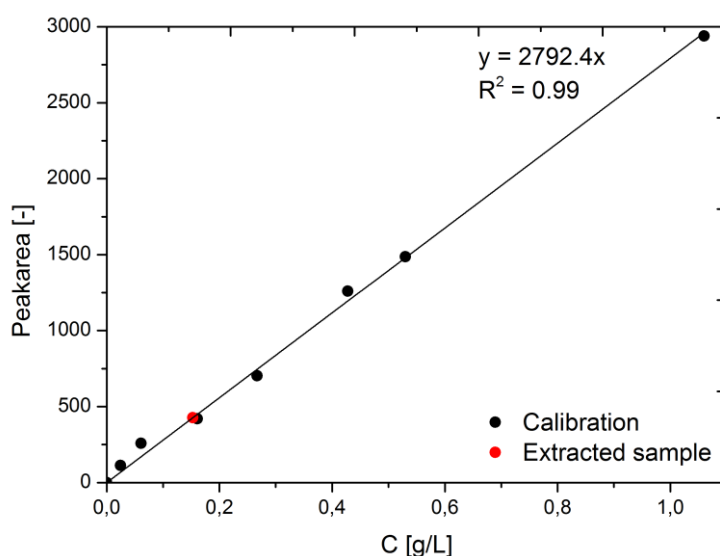| Sample	M_{PVA} [mg]	M_{epoxy} [mg]	m_{amine} [mg]	ΔH [J/g]	ΔH [J/g$_{Epoxy}$]
EA Bulk curing	-	5.89	6.87	106.3	230
PVA-EA bulk curing 3:1	12.07	1.89	2.26	26.6	228
PVA-EA bulk curing 1.25:1	10.76	3.92	4.66	47.0	232
PVA-EA fibres	3.53	0.41	0.49	16.7	192

Figure S6. Black: Calibration curve for the epoxide including linear regression and correlation coefficient. Red: Extracted sample after crosslinking of the amine and the PVA fibres with glutaraldehyde (GAH). The detected concentration corresponds to a recovery rate of 65 % epoxide under the assumption of quantitative extraction. The calculations include that the epoxide with a degree of polymerization of n = 0.15 carries OH-functionality which will be lost due to crosslinking with GAH.

Table S3. Parameters used for the computations.

R$_{Fibre}$ [nm]	r$_{EA}$ [nm]	f$_{EA}$	ρ$_{EA}$ [g/cm³]	ρ$_{PVA}$ [g/cm³]
155	75	0.284	1	1.19

$$f_{EA} = \frac{1}{(1 + \frac{3 * \rho_{EA}}{\rho_{PVA}})}$$

f$_{EA}$ represents the fraction of both amine and epoxy compartments compared to the total amount of polymers in the system (A&E + PVA). For this calculation it is assumed that the densities in the nanofibres equal those of the bulk polymers.

For the statistical evaluation of the nearest neighbour density probability 80000 moves were performed with a step size of 2.5 nm. The initial 40000 steps were discarded to avoid artefacts originating from the chosen starting conformation. The statistics were carried out on basis of the remaining 40000 steps.

[1] U. R. P. Schlichting, K. Müllen, *Liebigs Ann./Recueil* **1997**, 395-407.

[2] S. Banfi, E. Caruso, S. Zaza, M. Mancini, M. B. Gariboldi, E. Monti, *J. Photochem. Photobiol., B* **2012**, *114*, 52-60.

[3] L. M. Guerrini, M. P. de Oliveira, M. C. Branciforti, T. A. Custódio, R. E. S. Bretas, *Journal of Applied Polymer Science* **2009**, *112*, 1680-1687.