

Supporting Information

Self-Calibrating Mechanochromic Fluorescent Polymers Based on Encapsulated Excimer-Forming Dyes*Céline Calvino¹, Anirvan Guha¹, Christoph Weder^{1,*}, Stephen Schrettl^{1,*}*

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1. Supporting Data

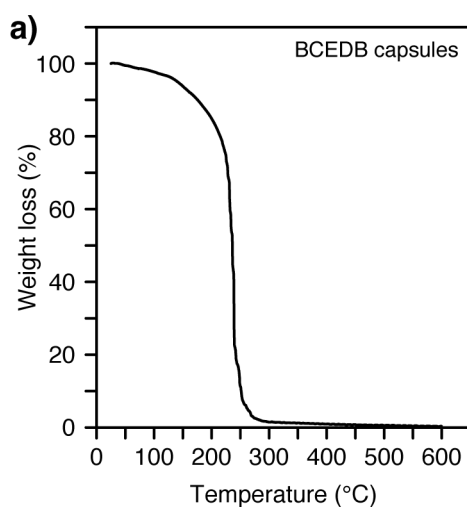


Figure S1. Thermogravimetric analysis (TGA) of the microcapsules. **a)** Thermogravimetric analysis of microcapsules filled with a solution of BCEDB in hexyl acetate.

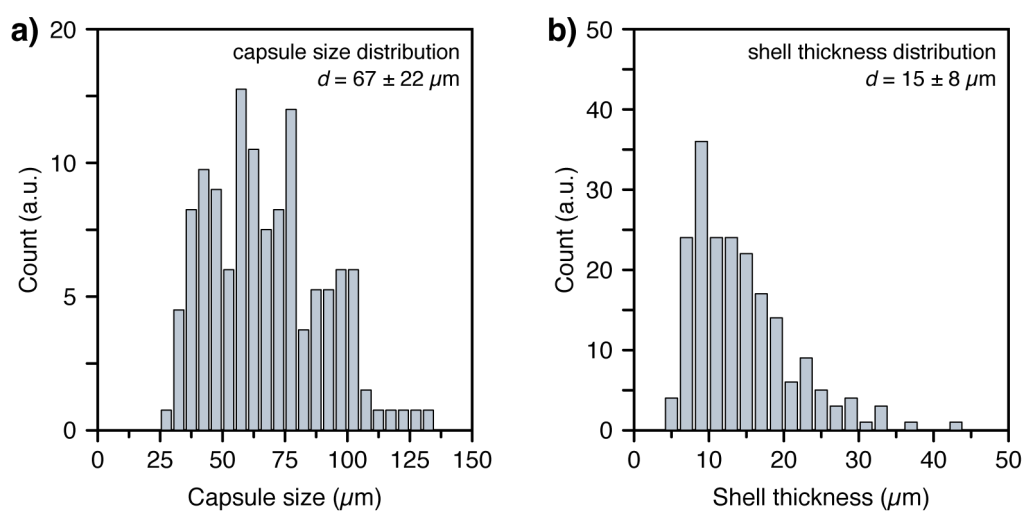


Figure S2. The capsule size distribution and shell thickness distribution were determined by measuring the diameter and shell thickness of individual capsules by analysis of optical microscopy images (evaluation of ca. 200 capsules). **a)** The particle diameter distribution of the microcapsules gave an average of $67 \pm 22 \mu\text{m}$. **b)** The shell thickness distribution of the microcapsules gave an average of $15 \pm 8 \mu\text{m}$.

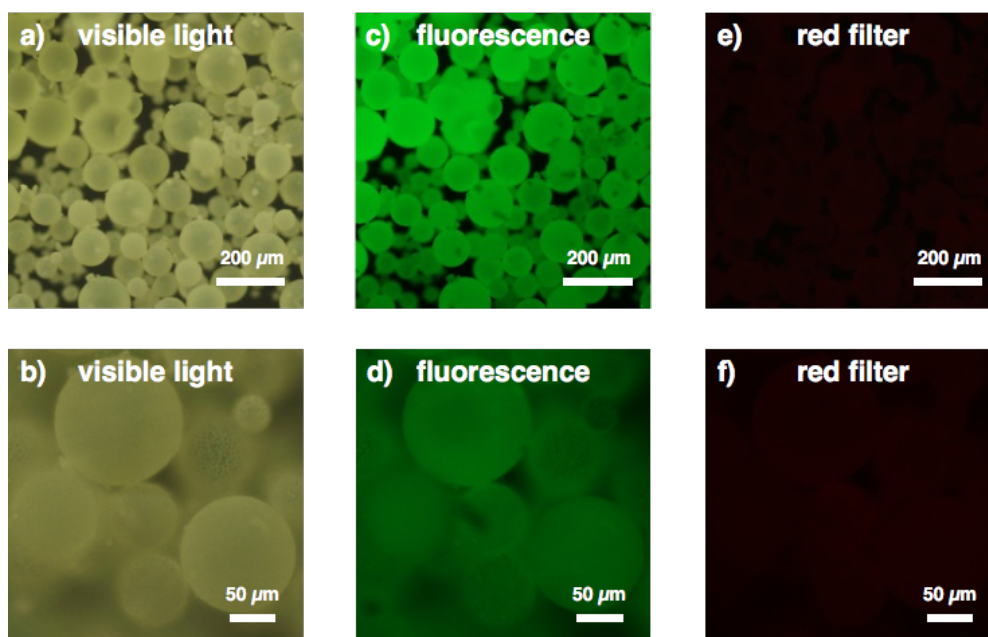


Figure S3. Optical and fluorescence microscopy images of capsules filled with a solution of BCEDB in hexyl acetate ($c = 6.4 \text{ mmol/L}$). Micrographs of capsules **a,b**) illuminated by visible light, **c,d**) illuminated by UV-light ($\lambda_{\text{ex}} = 365 \text{ nm}$), and **e,f**) under UV-light illumination ($\lambda_{\text{ex}} = 365 \text{ nm}$) with a red filter limiting emission to 580–630 nm.

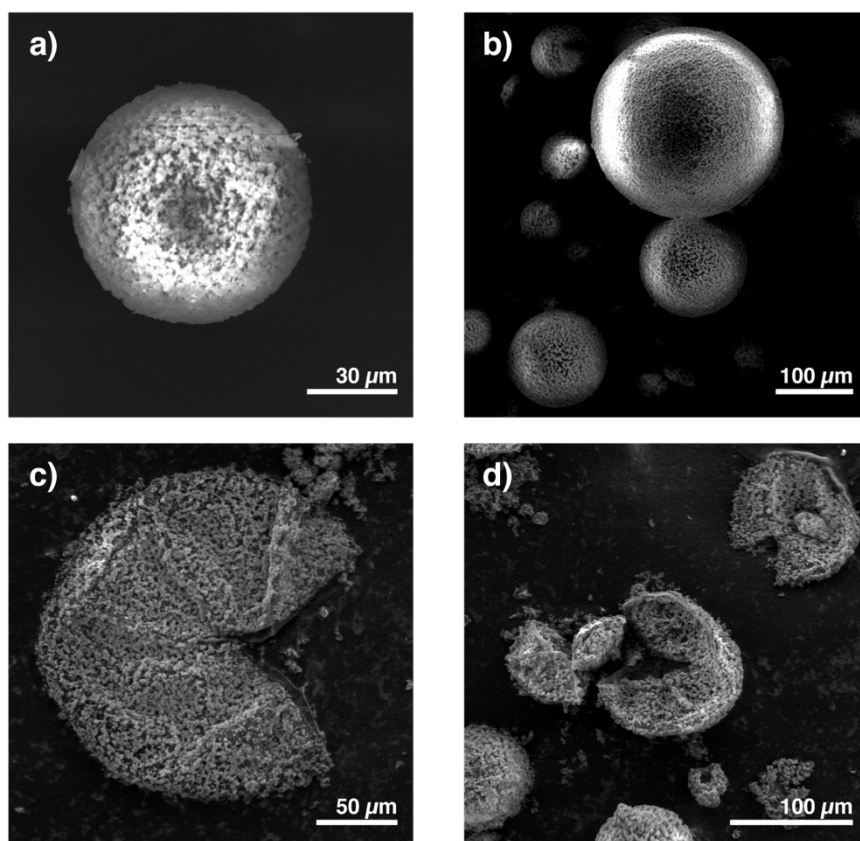


Figure S4. **a,b)** Scanning electron microscopy (SEM) of microcapsules with a poly(urea formaldehyde) shell that were obtained by the oil-in-water emulsion polycondensation of urea, resorcinol, and formaldehyde in the presence of 1-octanol and BCEDB dissolved in hexyl acetate. **c,d)** SEM micrographs recorded after mechanically crushing the microcapsules by compression between two glass slides and evaporation of the encapsulated solvent over the course of 30 min.

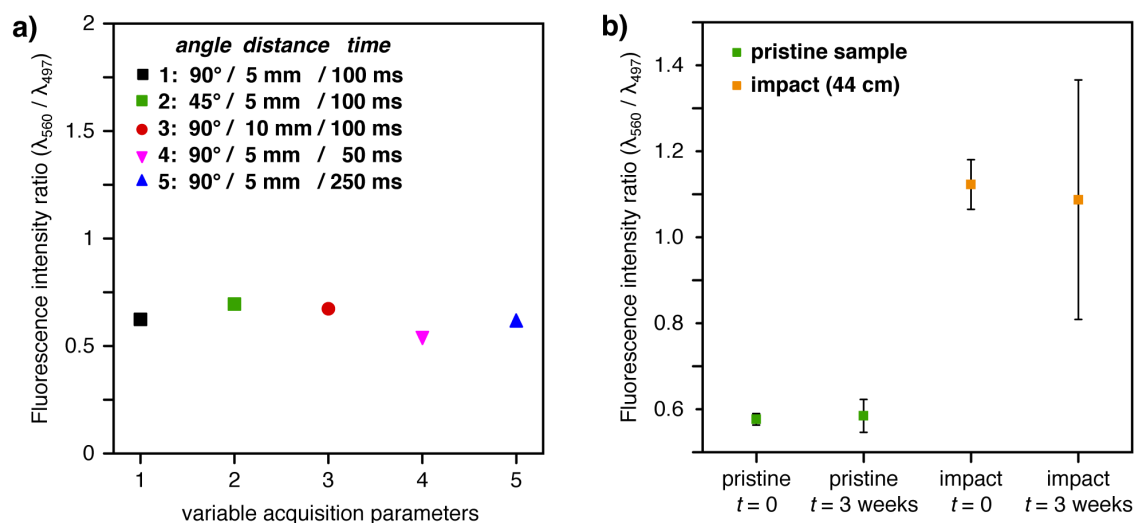


Figure S5. **a)** Plot of the ratio of the excimer to monomer emission intensities (I_E/I_M) recorded at 560 and 497 nm extracted from fluorescence spectra measured with different acquisition parameters (distance between fiber and sample, acquisition time, incidence angle of the optical fiber) showing that the intensity ratio remains constant independent of the acquisition parameters. **b)** Plot of the ratio of the excimer to monomer emission intensities (I_E/I_M) recorded at 560 and 497 nm extracted from fluorescence spectra measured with freshly prepared samples before and after application of mechanical stress (BCEDB microcapsule containing PDMS film; impact of a missile from 44 cm). The measurements were carried out with three distinct samples and repeated three weeks later showing that the intensity ratios remain constant over time. The shown intensity ratios are averages with standard deviation of the ratios obtained for the individual samples.

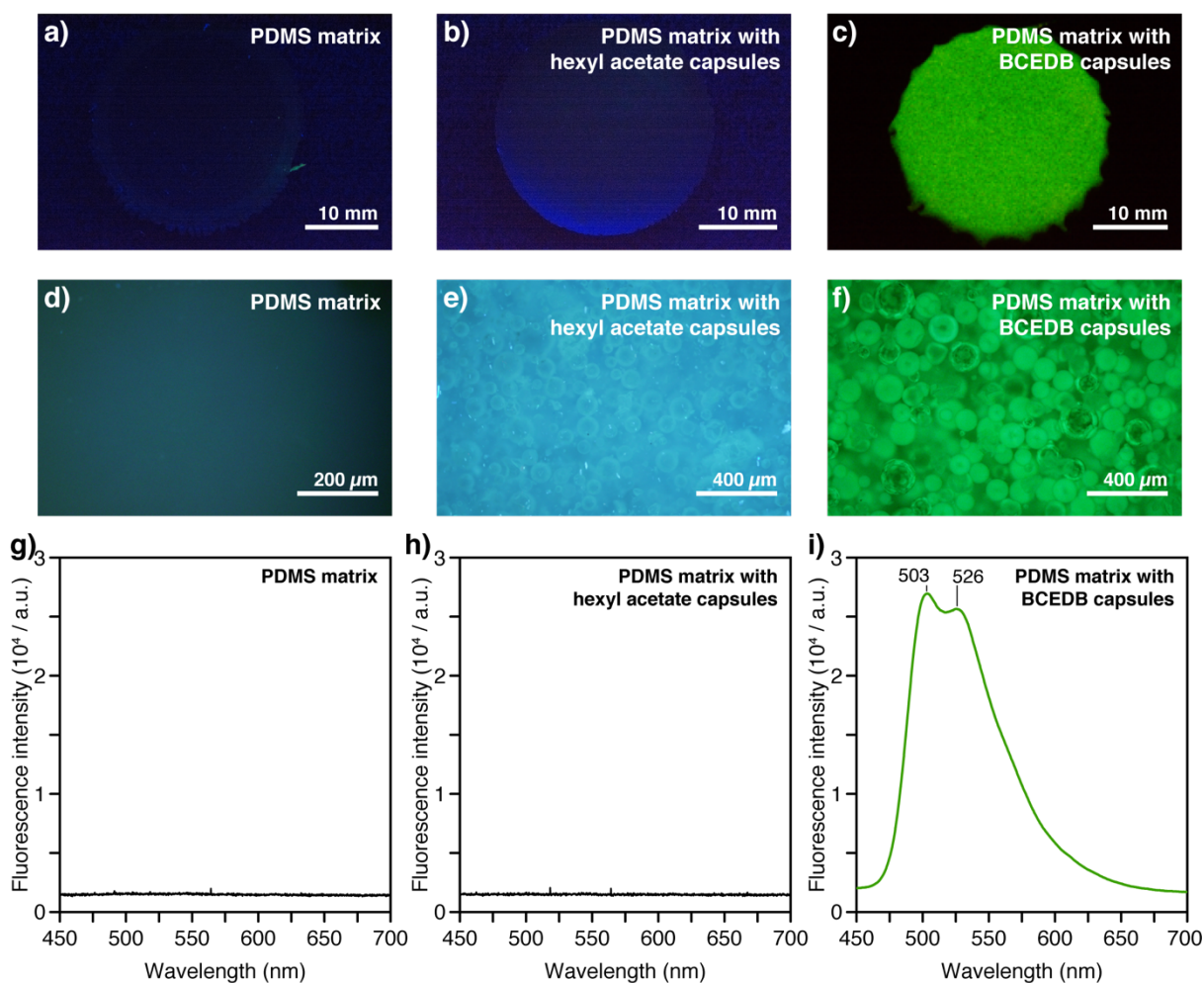


Figure S6. Pictures of a cured samples of (a) the poly(dimethoxysiloxane) (PDMS) matrix, (b) the PDMS matrix with embedded capsules containing hexyl acetate only, and (c) the PDMS matrix with embedded capsules filled with a hexyl acetate solution of the BCEDB chromophore (all recorded under illumination with UV-light ($\lambda = 365$ nm)). Fluorescence microscopy images of (d) the PDMS matrix (illuminated by reflected UV light ($\lambda = 365$ nm)), (e) the PDMS matrix with embedded capsules containing hexyl acetate (illuminated by reflected UV light ($\lambda = 365$ nm)), and (f) the PDMS matrix with embedded capsules filled with a hexyl acetate solution of the BCEDB chromophore (illumination with UV-light ($\lambda = 365$ nm)). Fluorescence spectra of (g) the PDMS matrix, (h) the PDMS matrix with embedded capsules containing hexyl acetate, and (i) the PDMS matrix with embedded capsules filled with a hexyl acetate solution of the BCEDB chromophore (in all cases with $\lambda_{\text{ex}} = 365$ nm).

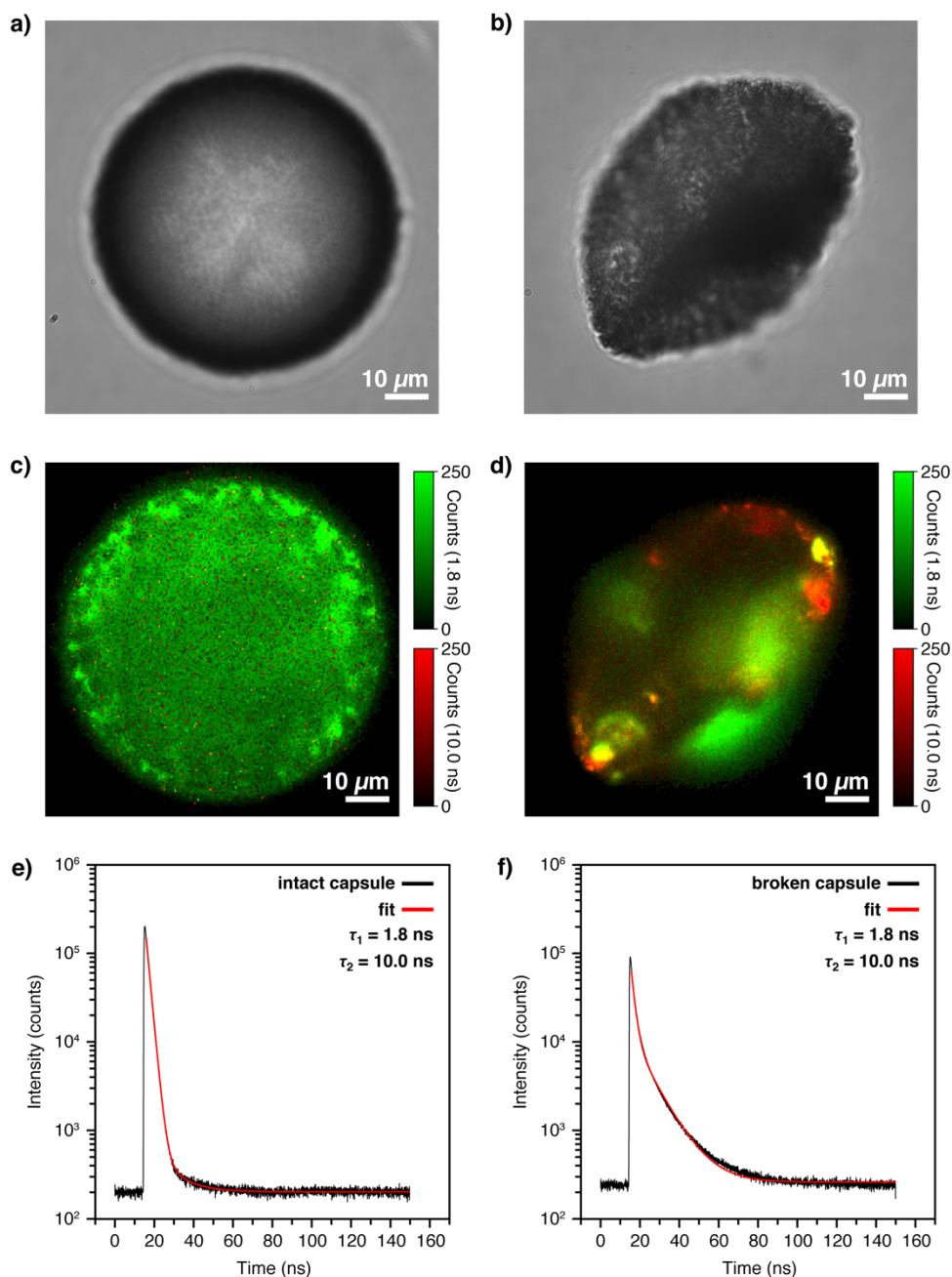


Figure S7. Bright-field microscopy images of (a) intact and (b) damaged microcapsules, as well as fluorescence lifetime images of the same (c) intact and (d) damaged microcapsules. Intensity scaling of lifetime color mapping is presented for both the monomer emission lifetime of 1.82 ns (green) and for the excimer emission lifetime of 10.0 ns (red). e) Overall fluorescence decay (black line) for the lifetime image of the intact capsule in (c) with the corresponding fit (red line). f) Overall fluorescence decay (black line) for the lifetime image of the damaged capsule in (d) with the corresponding fit (red line).

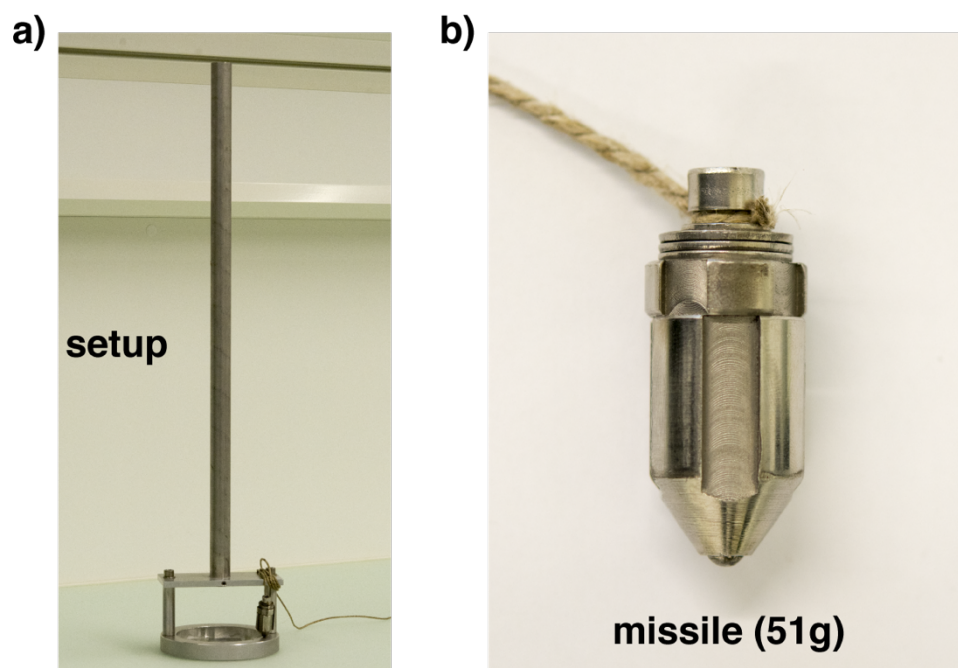


Figure S8. a) Picture of the setup for the impact experiments with a vertical tube that directs the missile at the sample. b) Picture of the missile that was employed as projectile for the impact experiments.

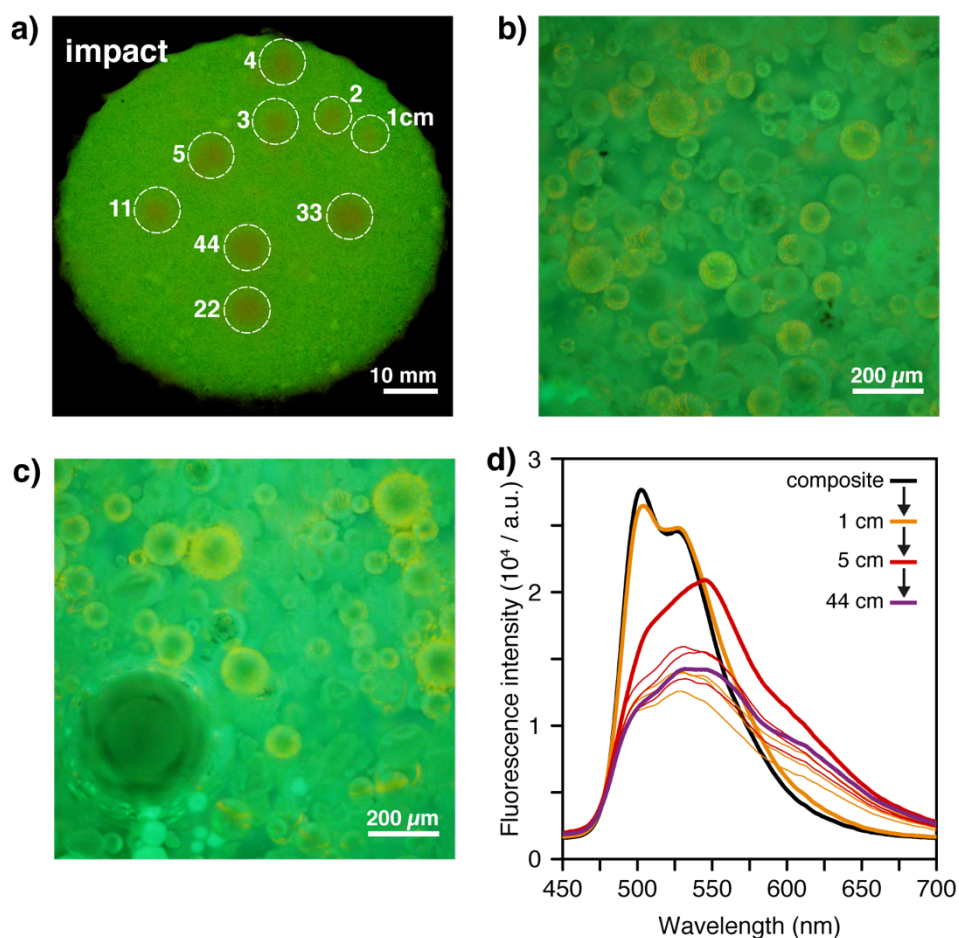


Figure S9. a) Picture of a cylindrical sample after exposure to impact of a missile from distances between 1 and 44 cm recorded under illumination with UV-light ($\lambda = 365$ nm). b,c) Fluorescence microscopy images of the damaged sample regions show the orange fluorescence of excimers next to the green fluorescence of the monomer ($\lambda = 365$ nm). d) Fluorescence spectra of the microcapsule-loaded PDMS composite recorded at the different positions that were exposed to impact from distances between 1 and 44 cm and used for the evaluation of the excimer to monomer emission intensities (I_E/I_M) (spectra were recorded with $\lambda_{\text{ex}} = 365$ nm).

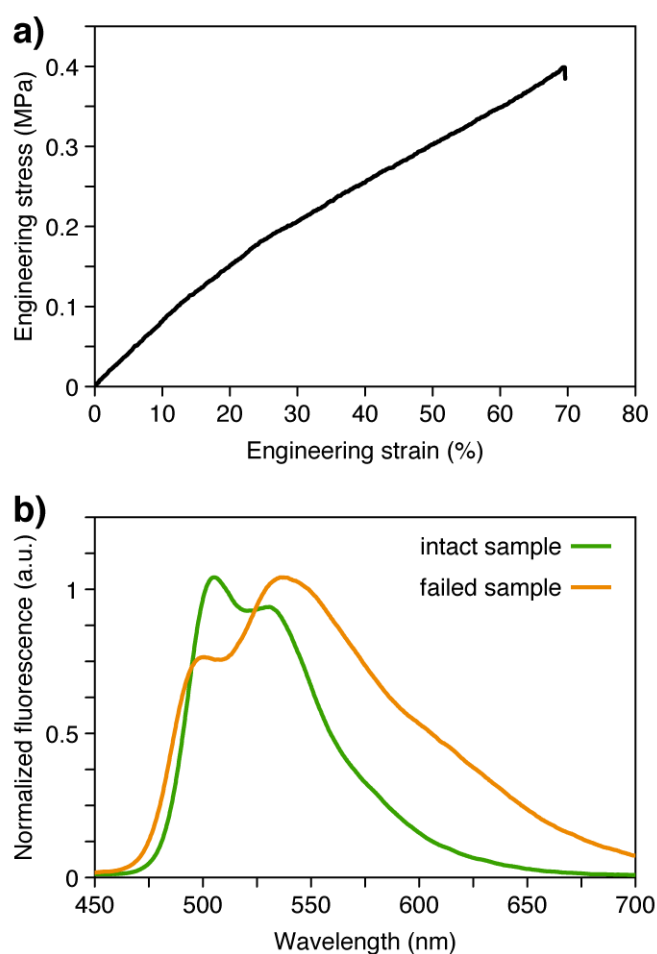


Figure S10. **a)** Plot of the engineering stress-engineering strain curve obtained upon tensile deformation of a dog-bone-shaped, microcapsule-loaded PDMS composite (10% w/w). **b)** Fluorescence spectra of dog-bone-shaped, microcapsule-loaded PDMS composite recorded after tensile deformation at the intact (green line) and failed (orange line) sample region. (spectra were in recorded with $\lambda_{\text{ex}} = 365 \text{ nm}$).

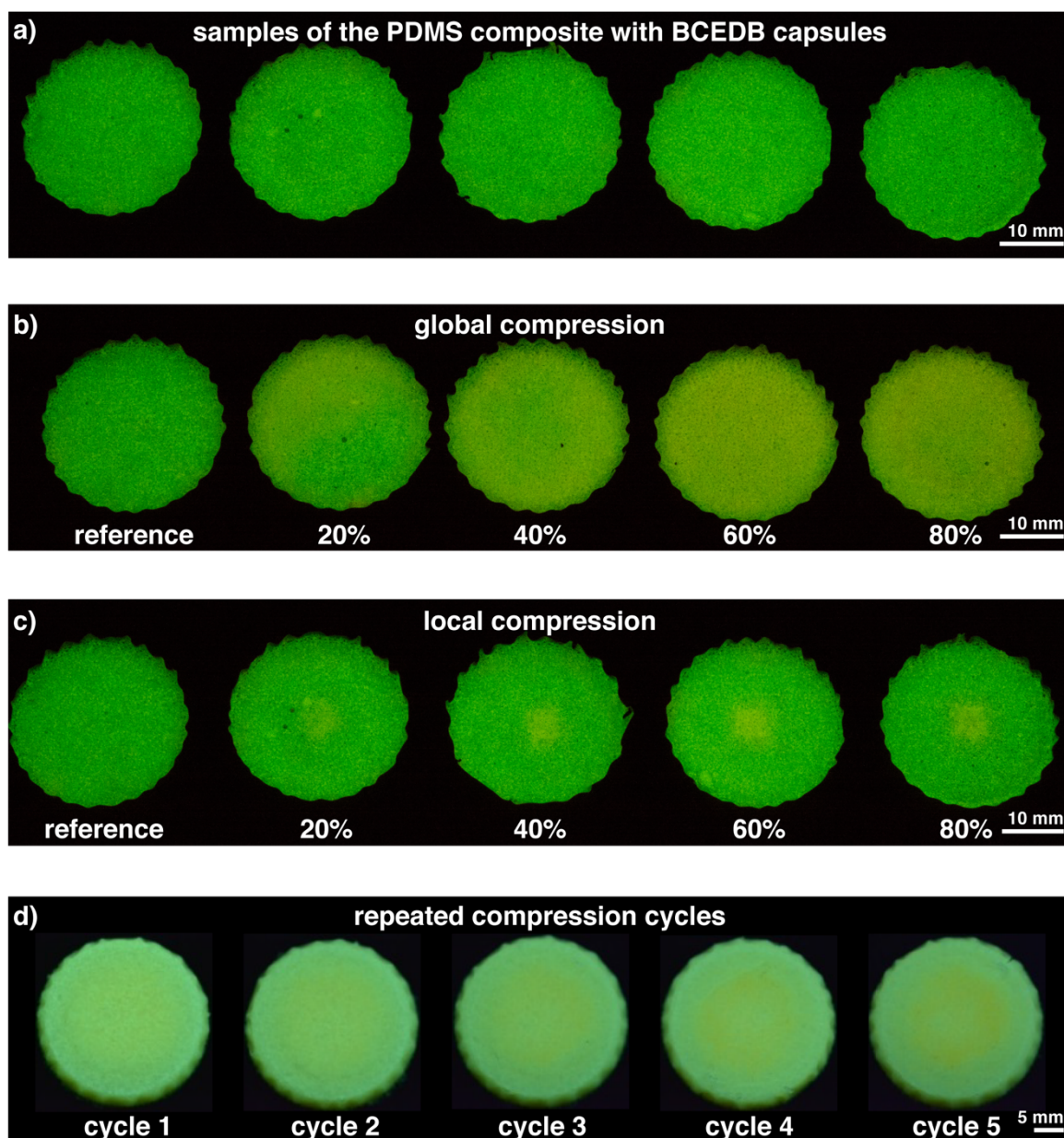


Figure S11. Pictures of samples of the PDMS composite with BCEDB capsules taken (a) before application of compressive stress, b) after global compression of the samples to compressive strains between 20–80%, c) after local compression of the samples to compressive strains between 20–80%, and d) after repeated compression to compressive strains of 60% (all pictures were taken under illumination with UV-light ($\lambda = 365$ nm)).

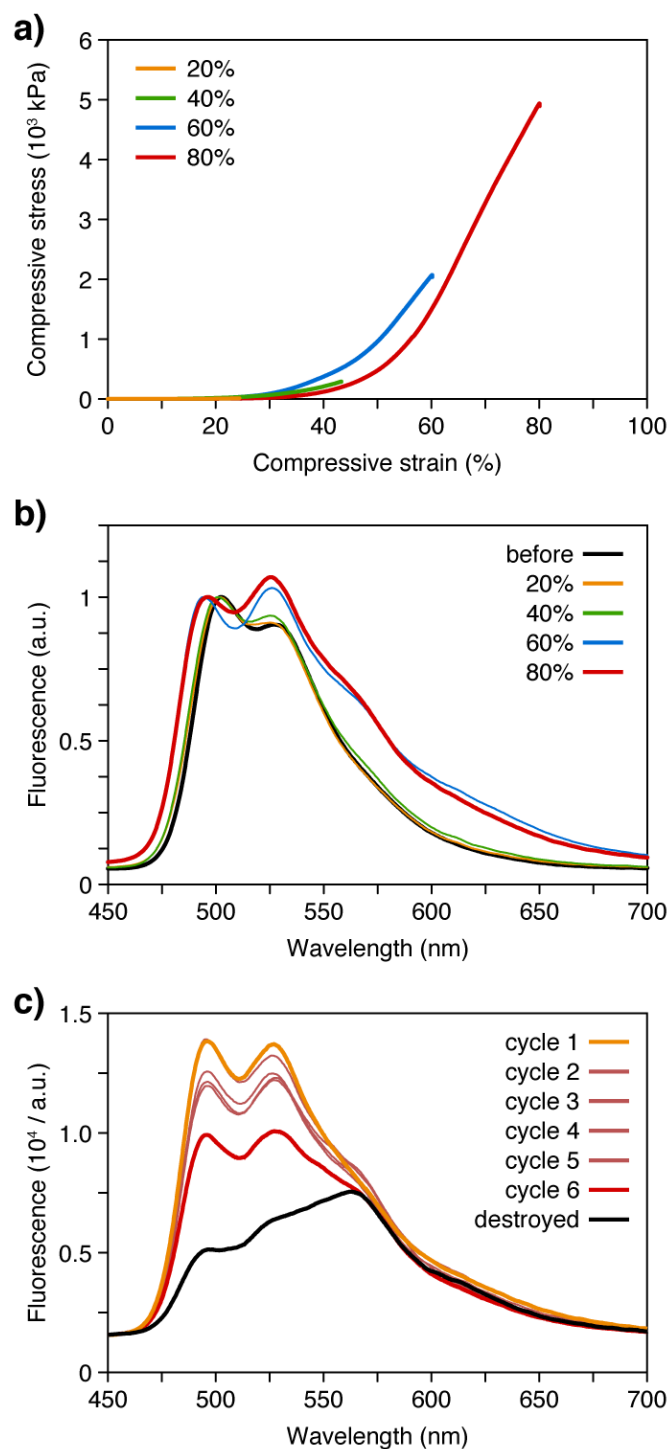


Figure S12. **a)** Compressive stress-strain measurements of PDMS/microcapsule composites with compression to strains of 20% (orange), 40% (green), 60% (blue), and 80% (red). **b)** Fluorescence spectra of PDMS/microcapsule composite after compression to strains of 20% (orange), 40% (green), 60% (blue), and 80% (red). **c)** Fluorescence spectra of PDMS/microcapsule composite recorded after repeated compression to compressive strains of 60%. (spectra were in all cases recorded with $\lambda_{\text{ex}} = 365$ nm).

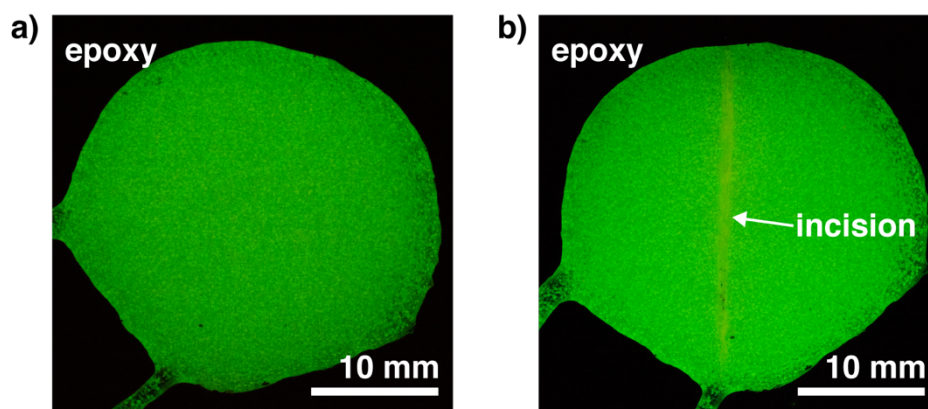


Figure S13. **a)** Picture of a cylindrical sample of a BCEDB microcapsule-loaded epoxy composite (10% w/w). **b)** Picture of the same epoxy composite taken 30 min after incision with a razor blade showing the orange excimer fluorescence (both photographs were taken under illumination with UV-light ($\lambda = 365$ nm)).

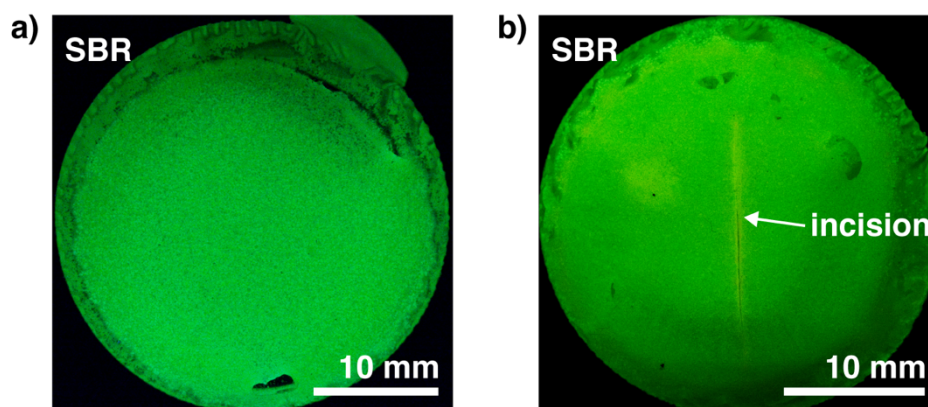


Figure S14. **a)** Picture of a cylindrical sample of a BCEDB microcapsule-loaded styrene-butadiene rubber composite (10% w/w). **b)** Picture of the same epoxy composite taken 30 min after incision with a razor blade showing the orange excimer fluorescence (both photographs were taken under illumination with UV-light ($\lambda = 365$ nm)).

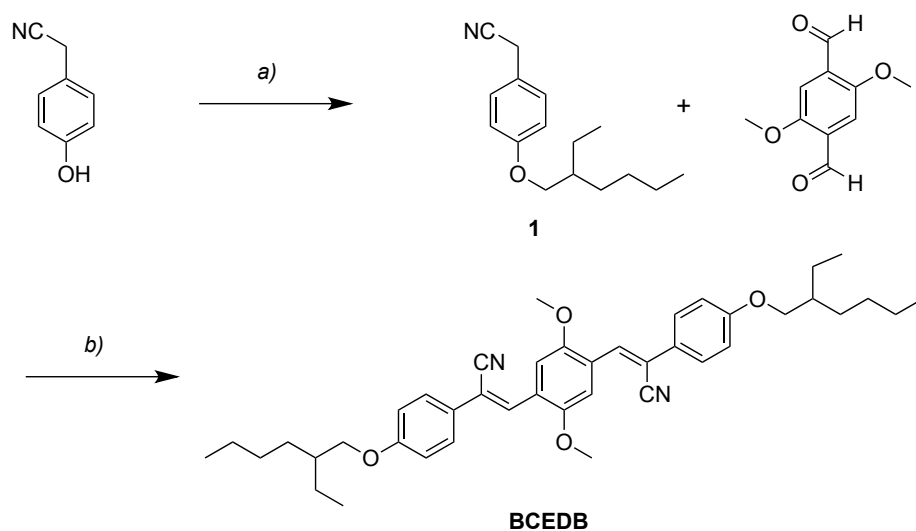


Figure S15. Schematic of the synthesis of 1,4-bis(α -cyano-4-(2-ethylhexyloxy)styryl)-2,5-dimethoxy-benzene (**BCEDB**). The reactions were carried out according to previously reported procedures.^[1] Reagents and conditions: (a) KOH, K₂CO₃, 2-ethylhexylbromid, DMF, 85°C, 4h, 54%; (b) t-butanol, t-BuOK in THF (1M), n-Bu₄NOH in MeOH (1M), THF, 70 °C, 15 min, 80%.

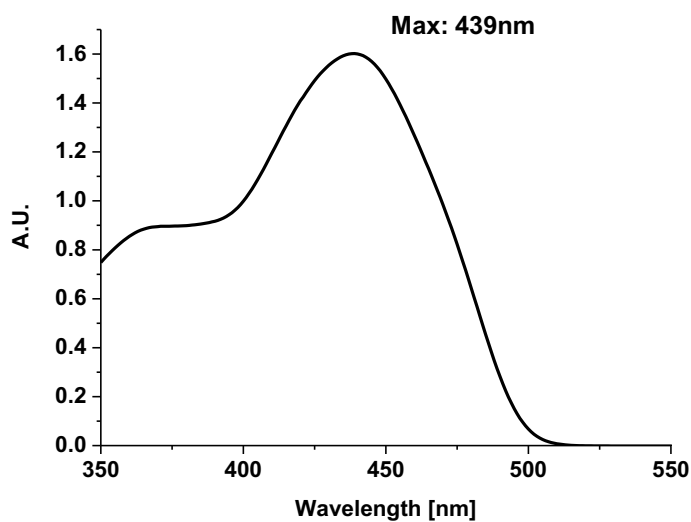


Figure S16. UV/Vis absorption spectrum of the 1,4-bis(α -cyano-4-(2-ethylhexyloxy)styryl)-2,5-dimethoxy-benzene (**BCEDB**) chromophore dissolved in hexyl acetate ($c = 36 \mu\text{mol/L}$, $\lambda_{\text{max}} = 439 \text{ nm}$).

2. Supporting Experimental Section

Materials. Urea, ammonium chloride, formaldehyde, resorcinol, 1-octanol, poly(ethylene-*alt*-maleic anhydride) (EMA) ($M_w = 500'000\text{--}1'000'000$ g/mol), poly(styrene-*b*-butadiene-*b*-styrene) rubber (SBR) (30% w/w styrene), Araldite[®] crystal, 2,5-dimethoxyterephthaldehyde, 4-hydroxyphenylacetonitrile, and all solvents were purchased as analytical grade from Sigma-Aldrich. All compounds and solvents were used without further purification. The elastomeric matrix composed of poly(dimethoxysiloxane) (PDMS) and Sylgard[®] 184 as a curing agent were supplied by Dow Corning.

Chemical Analytics. NMR Spectroscopy was carried out at 297.2 K on Bruker Avance DPX 400 or DPX 300 spectrometers at frequencies of 400.19 MHz or 300.23 MHz, respectively, for ¹H nuclei and 100.63 MHz or 75.49 MHz, respectively, for ¹³C nuclei. Spectra were calibrated to the residual solvent peak of CDCl₃ (7.26 ppm ¹H NMR; 77.16 ppm ¹³C NMR). Data were treated with MestReNova (11.0.4) software suite and all chemical shifts δ are reported in parts per million (ppm) with coupling constant in Hz (multiplicity: s = singlet, d = doublet, dd = double doublet, t = triplet, dt = doublet triplet, ddd = doublet doublet doublet, sep = septet, m = multiplet, br = broad signal). High resolution mass spectra (HRMS) were recorded as service measurements at the mass spectrometry service of the Institute of Chemistry of the University of Fribourg. ESI MS data were acquired on a Bruker FTMS 4.7T BioAPEX II equipped with a ComiSource 1.0 and operated in the positive ionization mode. Data were processed using Xmass 7.0.8 software. UV/Vis spectra were recorded on a JASCO V670 and data were acquired with the Spectra Manager software suite. Quartz cuvettes (1 cm) from Hellma were used to measure the absorption from 350–800 nm. Fluorescence spectroscopy measurements were performed on a Varian Cary Eclipse spectrometer using 1 cm quartz cuvettes. All fluorescence spectra of samples featuring the 1,4-bis(α -cyano-4-(2-ethylhexyloxystyryl))-2,5-dimethoxybenzene (**BCEDB**) derivative were recorded in the range

of 450–700 nm with an excitation wavelength of $\lambda_{\text{ex}} = 438$ nm. Fluorescence spectra of solid samples were recorded with an Ocean Optics USB4000-FL spectrometer under excitation at $\lambda_{\text{ex}} = 370$ nm from an Ocean Optics LS-450 LED light source using an Ocean Optics Shimadzu UV-2401 PC optical fiber in reflection geometry. The samples were placed on a substrate and the optical fiber was oriented normal to surface at a distance of 5 mm, resulting in a spot size of approximately 800 μm from which the diffuse reflectance was measured. Spectra were recorded before and after the application of mechanical stress and data were acquired with Stream basic software.

Fluorescence and Optical Microscopy. Images were acquired using an Olympus BX51 microscope equipped with DP72 digital camera. Photographs and size measurements of the microcapsules were carried out using the Stream Basic software suite. Fluorescence microscopy images were acquired on the same microscope under illumination of a X-Cite 120Q wide-field fluorescence excitation light source.

Fluorescence Lifetime Imaging Microscopy. Fluorescence lifetime imaging microscopy (FLIM) of single intact and damaged microcapsules were collected using an inverted-type laser scanning confocal microscope (MicroTime 200, Picoquant GmbH, Germany) with an Olympus UPlanSApo water immersion objective (60x, 1.2 NA). Samples were excited by a 440 nm pulsed-diode laser at 6.67 MHz repetition rate. A Chroma ZT442rdc-UF3 main dichroic and a Semrock AT 465 long pass filter were used to attenuate the fluorescence signal and direct it to an Excelitas Technologies SPCM APD detector. Each FLIM image was 200×200 pixels, collected with a dwell time of 70 ms per pixel. SymPhoTime 64 software (Picoquant GmbH, Germany) was used to extract lifetime values from multi-exponential fits of the overall fluorescence decay of each image and color map the image pixels to representative lifetime values. Accompanying bright-field microscopy images were taken with an iDS uEye camera.

Scanning Electron Microscopy (SEM). Microcapsules were directly placed on the carbon adhesive tape on top of a metallic SEM sample holder. SEM images were recorded with a TE Scan Mira 3 microscope operating between 5–10 kV.

Thermogravimetric analysis (TGA). Measurements were conducted under a N₂ atmosphere using a Mettler-Toledo STAR thermogravimetric analyzer in the range from 25 to 600 °C with a heating rate of 10 °C/min.

Photography. Photographs were taken with a Nikon D7100 digital camera equipped with a AF-S DX Zoom-NIKKOR 18-135mm lens (f/3.5-5.6G IF-ED).

Color analysis. RGB color analysis was carried out on 32 bit photographs using the Fiji software. For one defined area the red, green, and blue color channels were split. In the corresponding region of interest, pixel intensity was averaged to provide a mean value for the respective channels. Red and green mean value were extracted and their ratio was calculated. For the evaluation of each sample in impact experiments, three measurements were taken for every impact distance and averaged. The analysis was carried out in the same way for the compression experiments. For the evaluation of samples in tensile experiments, three separate vertical lines were drawn along the longitudinal axis of the dog-bone-shaped specimen, measurements at defined distances from the rupture point were performed along these lines, and the values for every distance were averaged. Photographs of the samples containing 4800 × 3200 pixels were employed and measurements were performed in a window of 50 × 50 pixels in the region of interest.

Preparation of Poly(urea-formaldehyde) Microcapsules. The preparation of poly(urea-formaldehyde) (PUF) microcapsules was performed following previously reported procedures.^[2,3] In a 500 mL round-bottom flask, poly(ethylene-*alt*-maleic anhydride) (0.67 g) was dissolved in deionized water (125 mL) and urea (2.5 g), resorcinol (0.25 g), and

ammonium chloride (0.25 g) were successively added. The pH of the solution was then adjusted to 4 by dropwise addition of 1M aqueous sodium hydroxide solution and one drop of 1-octanol was added to the mixture. Thereafter, a solution of **BCEDB** (211 mg) in 60 mL of hexyl acetate was slowly added. The mixture was stirred for 10 min, formaldehyde (6.3 g) was added, and the temperature was increased to 55 °C. The reaction mixture was stirred with a RW 20 digital mechanical stirrer equipped with an overhead stirrer shaft with two movable paddles with a diameter of 60 mm at 450 rpm for 4 h, stirring was stopped, the mixture was allowed to cool to room temperature, and the suspension was left to settle overnight. The obtained microcapsules were filtered over a Büchner funnel, thoroughly rinsed successively with water, acetone, and dichloromethane (DCM), and thereafter left to dry for 24 h in air.

Preparation of Microcapsule Composites. Polydimethylsiloxane composites were prepared by mixing the matrix (Sylgard[®] 184) in the recommended ratio of 10 parts of the silicone base to 1 part of the curing agent with the desired total amount of the microcapsules (10% w/w). The mixture was carefully stirred to obtain a homogenous distribution of the capsules, poured into the desired container (e.g. aluminum or polytetrafluoroethylene (PTFE) mold), and cured by heating to 80 °C for 40 min in an oven. In this way, composite samples of different sizes and shapes were prepared for the different experiments. Epoxy composites were prepared by mixing in an aluminum mold commercial two-component Araldite[®] crystal adhesive with the desired total amount of microcapsules (10% w/w). The mixture was carefully stirred to obtain a homogenous distribution of the capsules and cured at ambient temperature for 15 min. Removal from the mold furnished cylindrical epoxy samples with an average diameter of 28 mm and a thickness of 6.3 mm. Poly(styrene-butadiene) rubber composites were prepared by dissolving commercial SBR (poly(styrene-*b*-butadiene-*b*-styrene); 30% w/w styrene) in a ten-fold volume excess of chloroform (e.g., 1 g SBR / 10 mL CHCl₃). The solvent was evaporated in ambient conditions until a highly viscous mixture was obtained to which the

microcapsules (10% w/w) were added, the mixture was carefully stirred, and transferred to an aluminum mold. After drying in ambient conditions for 8 h, the residual solvent was removed by drying for 3 h in high vacuum. Removal from the mold furnished cylindrical SBR samples with an average diameter of 28 mm and a thickness of 6.3 mm.

Characterization of the Microcapsules. Optical microscopy was used to measure the microcapsules' average diameter and shell thickness. These values and standard deviations were determined by analyzing images of 200 capsules. The weight fraction of the shell was determined by mechanically crushing BCEDB filled microcapsules (518 mg) using a mortar and pestle. The crushed capsules were placed in a beaker with chloroform (50 mL), the shell suspension was filtered, and thoroughly washed with chloroform to separate the solid residue from the dissolved BCEDB. After drying in vacuum, the shell fragments were weighed (24 mg) and a weight percentage of the BCEDB/hexyl acetate cargo of 95% w/w was determined.

Mechanical Testing. Compression and tensile deformation measurements were performed at ambient conditions using a Zwick/Roell Z010 tensile tester equipped with a 10 kN load cell. Dog-bone samples were prepared in a mold with a cross section of $4 \times 7 \times 10$ mm. Uniaxial tensile experiments were performed at a rate of 1 mm/min by using DIN EN ISO 527-1 test standard. The sample was photographed before and after mechanical measurements. Cylindrical samples for compression testing were prepared with an average diameter of 28 mm and a thickness of 6.3 mm in cylindrical aluminum molds. Compressive strains from 0–80% were applied for 2 minutes on every sample with a compression rate of 1 mm/min. The samples were photographed before and after mechanical measurements in order to monitor the fluorescence change according to the applied compressive stress. In the same way, cylindrical samples with a thickness of 1 mm and a diameter of 28 mm were also prepared and global compression to different compressive strains was carried out. For local

compression experiments, a small rectangular metal cube with dimensions of $0.5 \times 0.5 \times 0.5$ mm was placed on the surface of the sample before the compression experiment. Impact tests were performed with a conical missile (51 g) that was dropped through a tube from varying distances onto the sample. Cylindrical samples for impact tests were prepared with an average diameter of 70 mm and a thickness of 6.3 mm in cylindrical aluminum molds. For all experiments, the delay between application of mechanical stress and sample inspection was a fixed period of 30 min in order to allow for an efficient dispersion/evaporation of the solvent and excimer formation. Samples were kept under ambient conditions without applied mechanical stress during this period and characterization was carried out subsequently.

Synthesis of 4-(2-ethyl(hexyl)oxy)phenylacetonitrile 1. In a 100 mL round-bottom flask, potassium carbonate (8.10 g, 58.4 mmol) was added to 45 mL of dimethylformamide, the mixture was purged with nitrogen for 15 min, heated to 80 °C, and 4-hydroxyphenylacetonitrile was added (2.94 g, 22 mmol). After 10 min, 2-ethylhexylbromide (5.5 g, 28.4 mmol) was added dropwise to this mixture. The suspension left stirring under a nitrogen atmosphere at 100 °C for 4 h, after which the pale-yellow suspension was poured into ice-water (300 mL), extracted three times with dichloromethane (3×100 mL), the organic phases were combined, washed three times with water, and once with saturated NaCl solution. The organic phase was dried over MgSO_4 , filtered, and concentrated *in vacuo* to yield a yellowish oil. Purification by column chromatography column (silica gel, hexane/ethyl acetate 9:1) yielded **1** (2.95 g, 12 mmol, 54%) as colorless oil.

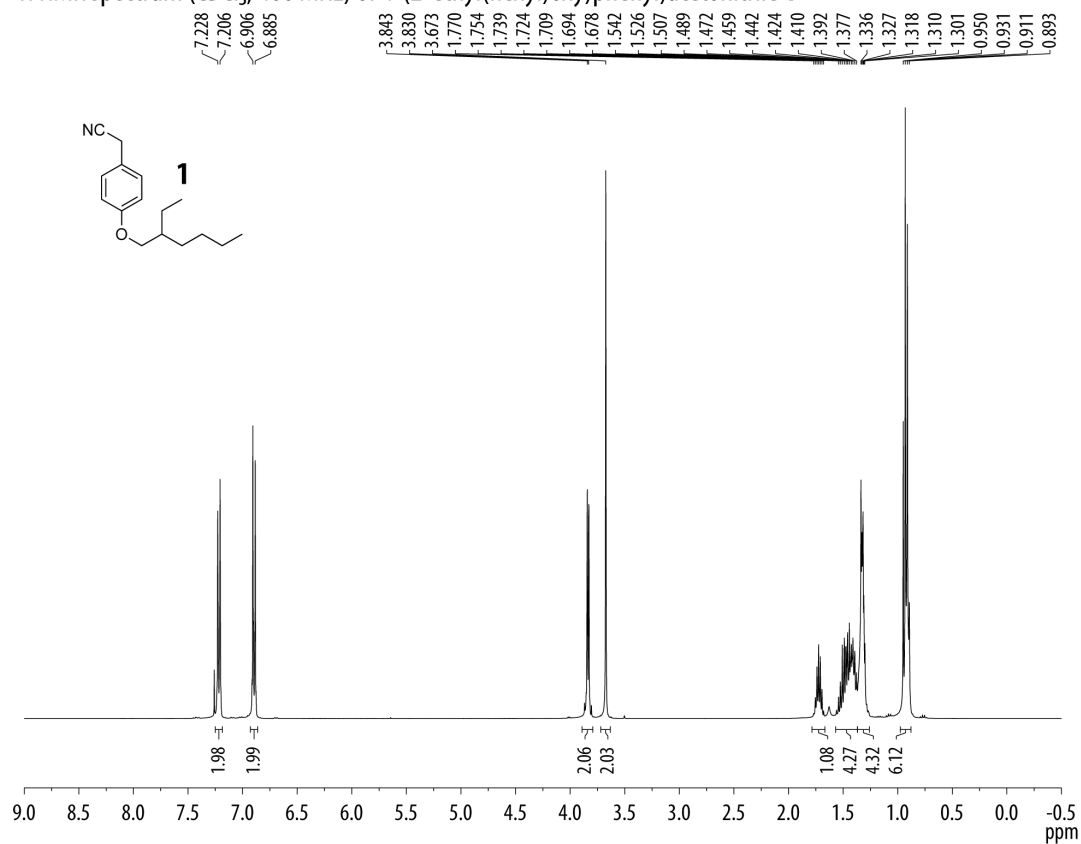
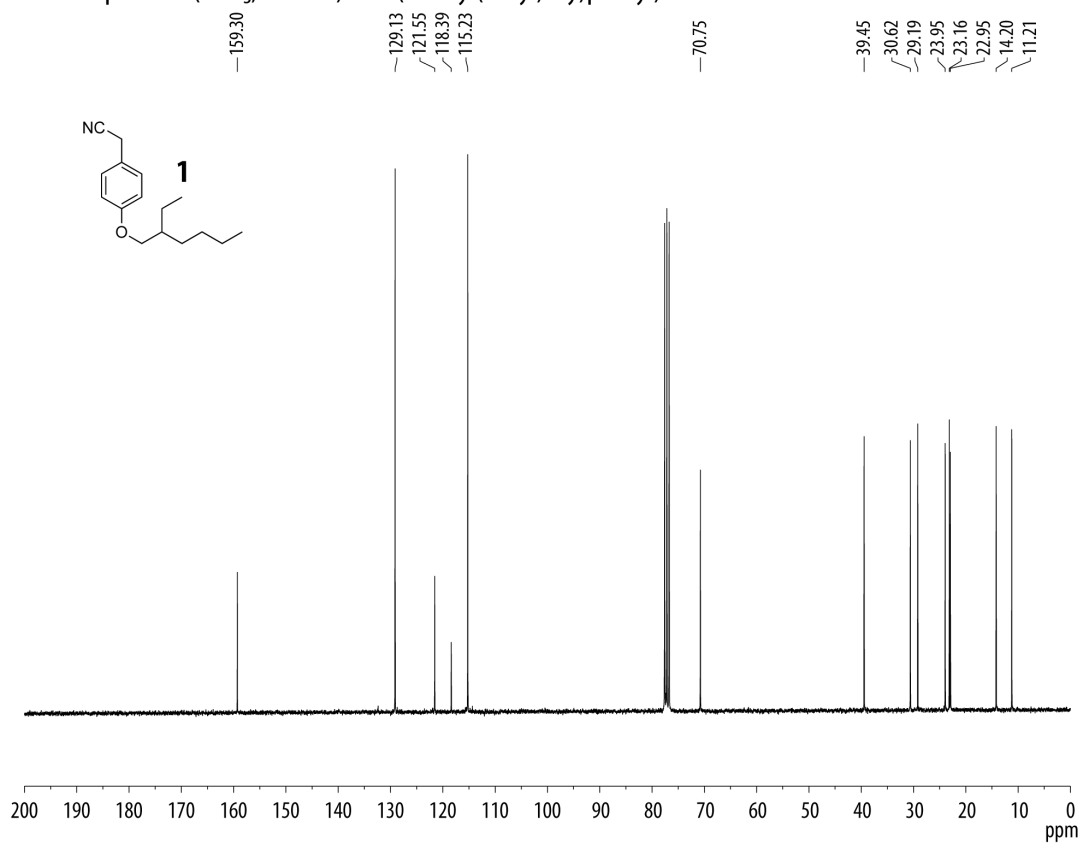
^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.23–7.21 (m, 2H, PhH), 6.91–6.88 (m, 2H, PhH), 3.84–3.83 (m, 2H, OCH_2), 3.67 (s, 2H, CNCH_2), 1.73 (sep, $J = 6.1$ Hz, 1H, CH), 1.54–1.38 (m, 4H, 2 CH_2), 1.34–1.30 (m, 4H, 2 CH_2), 0.95–0.89 (m, 6H, 2 CH_3). ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) = 159.3 (COCH_2), 129.1 (2C, C-Ar), 121.6 (C-Ar), 118.4 (CN), 115.2 (2C, C-Ar), 70.8 (OCH_2), 39.5 (CH), 30.6, 29.2, 24.0, 23.2, 23.0 (5C, CH_2), 14.2, 11.2 (2C, CH_3).

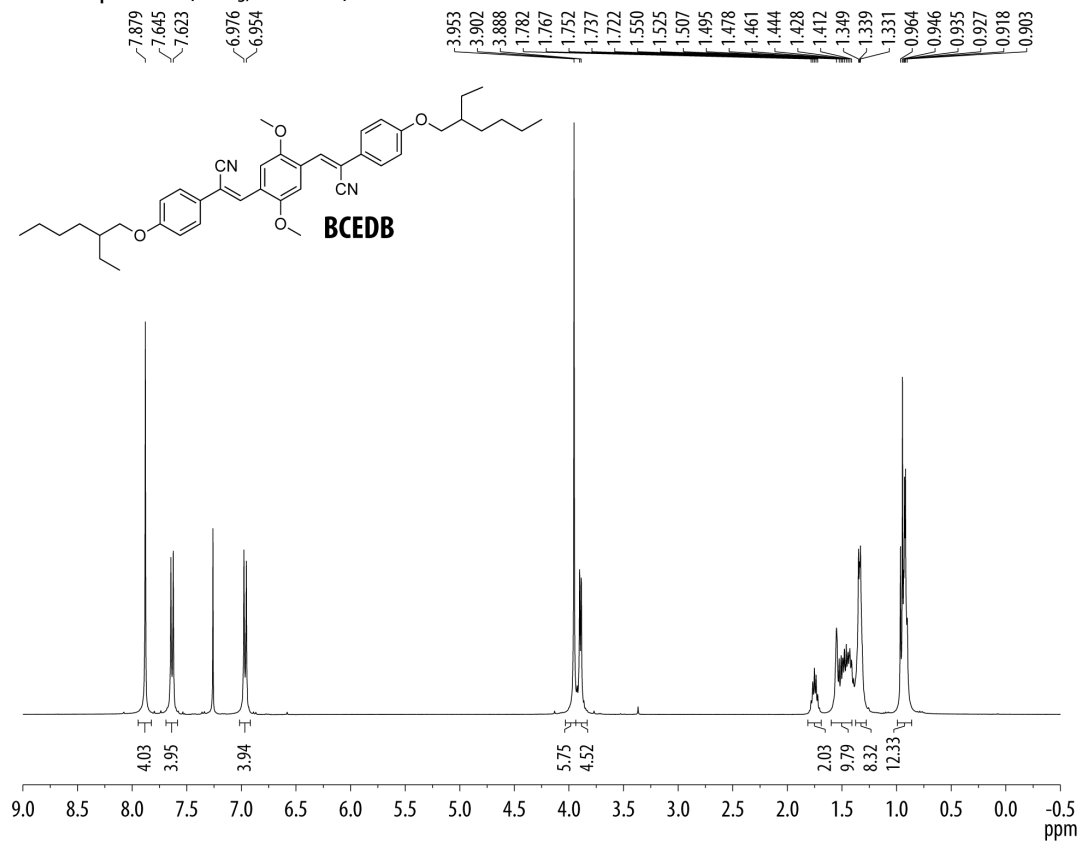
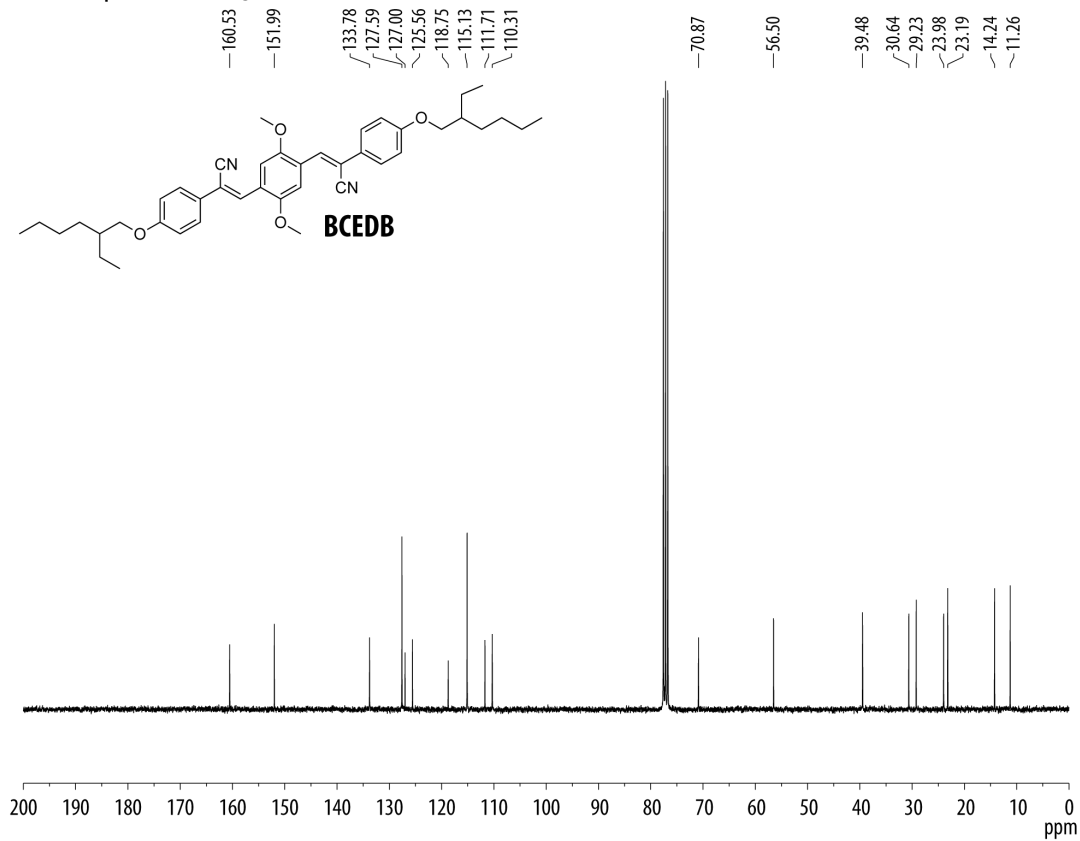
Synthesis of 1,4-bis(α -cyano-4-(2-ethylhexyloxystyryl))-2,5-dimethoxybenzene (BCEDB).

4-(2-Ethyl(hexyl)oxy)phenyl)acetonitrile **1** (1 g, 4 mmol) and 2,5-dimethoxyterephthaldehyde (0.315 g, 1.2 mmol) were dissolved at 70 °C in a mixture of *tert*-butanol (29 mL) and tetrahydrofuran (9 mL). Potassium *tert*-butoxide (0.24 mL, 1M in THF, 0.24 mmol) and tetrabutylammonium hydroxide (1.15 mL, 1M in MeOH, 1.15 mmol) were quickly added to the stirred solution. The reaction was allowed to stir for 15 min at 70 °C, after which the obtained deep red solution was cooled to room temperature and poured into an acidified MeOH solution (ca. 10 drops of acetic acid in 450 mL of MeOH). The orange precipitate was filtered through a paper filter, thoroughly washed with MeOH, and dried *in vacuo*. The crude compound was dissolved in CHCl₃, precipitated in hexane, and the orange precipitate was collected by filtration through a paper filter to yield **BCEDB** (630 mg, 0.97 mmol, 80%) as an orange solid.

¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.88 (s, 4H, 2 PhH, 2 =CH), 7.64–7.62 (m, 4H, PhH), 6.98–6.95 (m, 4H, PhH), 3.95 (s, 6H, OCH₃), 3.90 (d, 4H, 2 OCH₂), 1.75 (sep, *J* = 5.9 Hz, 2H), 1.55–1.41 (m, 10H, 5 CH₂), 1.35–1.33 (m, 8H, 4 CH₂), 0.96–0.90 (m, 12H, 4 CH₃).
¹³C NMR (75 MHz, CDCl₃) δ (ppm) = 160.5, 152.0 (4C, 2 COCH₃, 2 COCH₂), 133.8 (2C), 127.6 (2C), 127.0 (4C), 125.6 (2C), 118.8 (2C), 115.1 (4C), 111.7 (2C), 110.3 (2C), 70.9 (2C, PhOCH₂), 56.5 (2C, PhOCH₃), 39.5 (2C, CH), 30.6, 29.2, 24.0, 23.2 (8C, CH₂), 14.2, 11.3 (4C, CH₃).

3. Supporting Molecular Characterization

¹H NMR spectrum (CDCl₃, 400 MHz) of 4-(2-ethyl(hexyl)oxy)phenylacetonitrile **1**¹³C NMR spectrum (CDCl₃, 75 MHz) of 4-(2-ethyl(hexyl)oxy)phenylacetonitrile **1**

¹H NMR spectrum (CDCl₃, 400 MHz) of **BCEDB**¹³C NMR spectrum (CDCl₃, 75 MHz) of **BCEDB**

4. Supporting References

- [1] B. R. Crenshaw, C. Weder, *Chem. Mater.* **2003**, *15*, 4717.
- [2] A. Lavrenova, J. Farkas, C. Weder, Y. C. Simon, *ACS Appl. Mater. Interfaces* **2015**, *7*, 21828.
- [3] E. N. Brown, M. R. Kessler, N. R. Sottos, S. R. White, *J. Microencapsulation* **2010**, *20*, 719.