Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Strain-correlated mechanochromism in different polyurethanes featuring a supramolecular mechanophore

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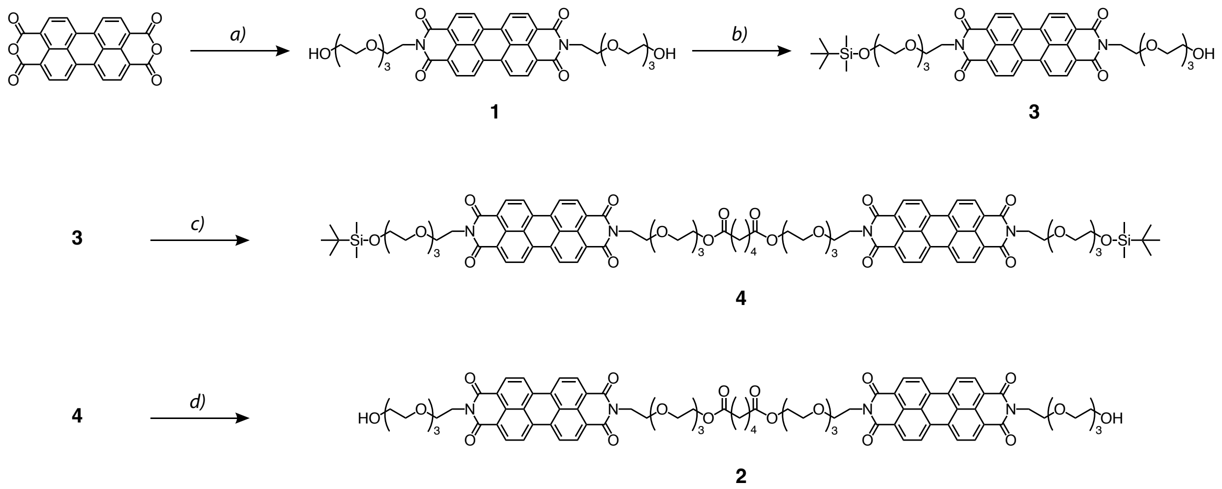
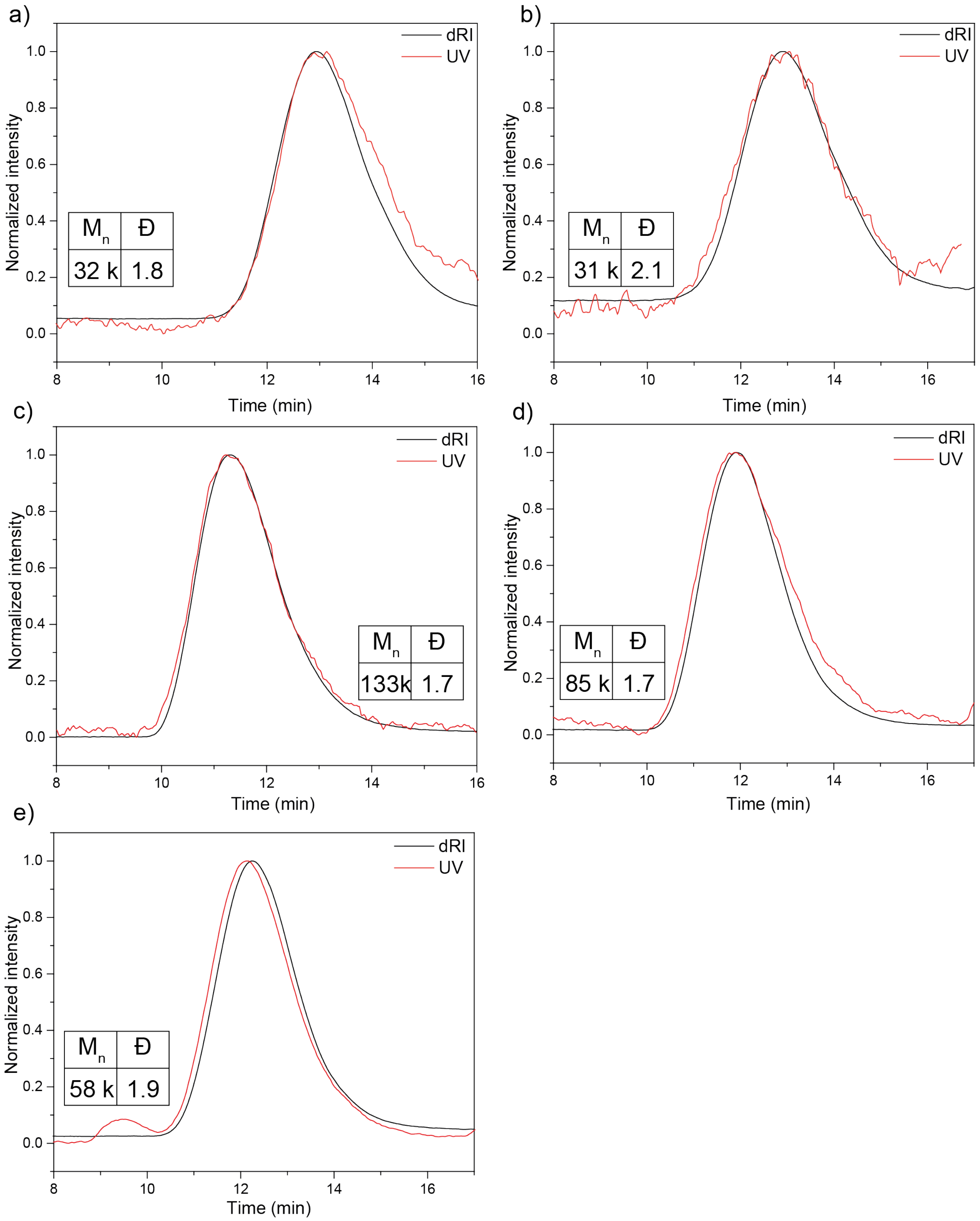
Table of Contents

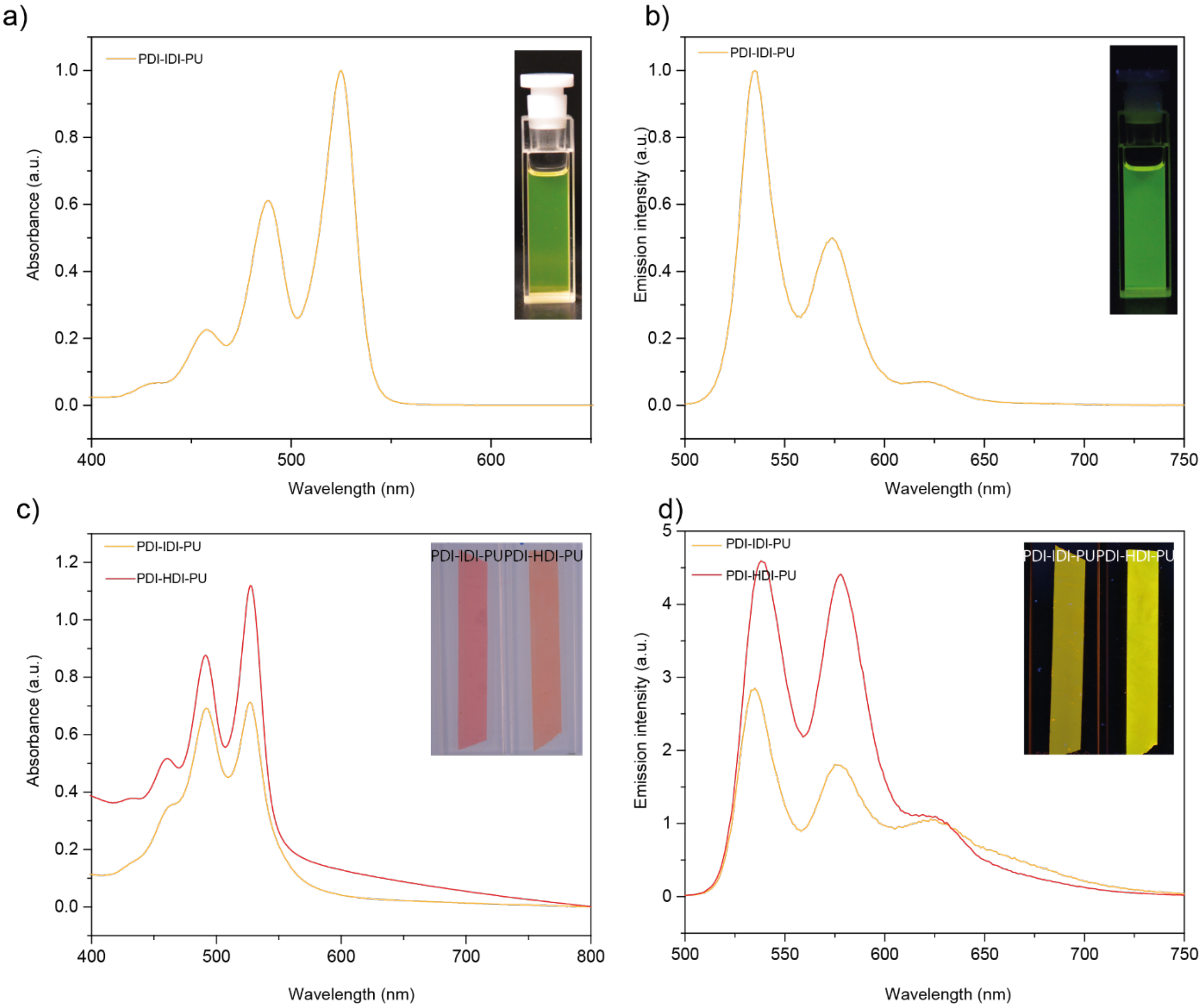
1. Supplementary Figures S1–S17



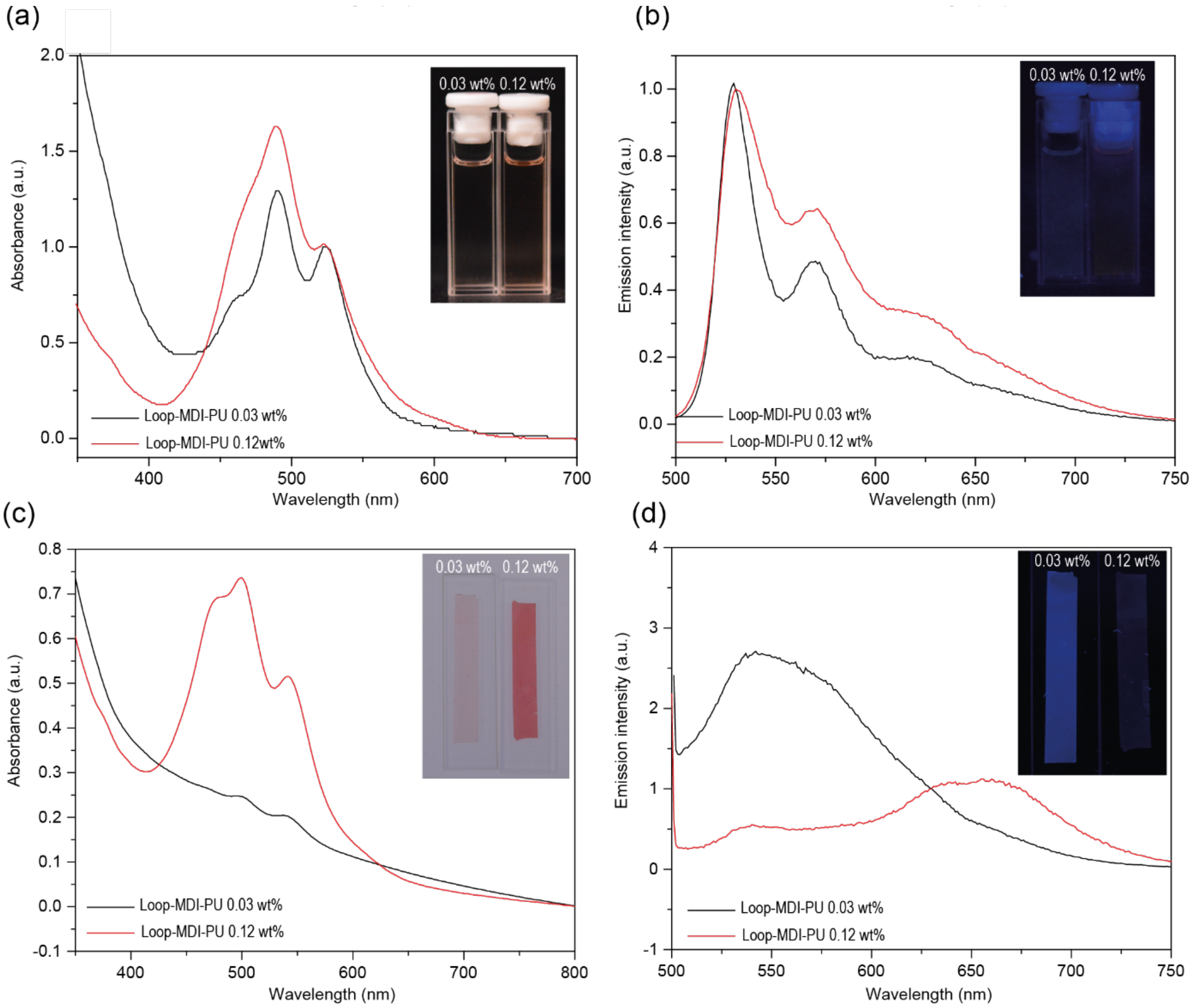
Supplementary Figure S1. Synthesis of a monomeric perylene diimide derivative **1** with hydroxyl groups at each terminus and the loop-forming mechanophore motif **2**. *Reagents and conditions*: *a*) 2-(2-(2-(2-aminoethoxy)ethoxy)ethoxy)ethanol, dimethylformamide (DMF), 200 °C, 77%; *b*) pyridine, 4-dimethylaminopyridine (DMAP), *tert*-butyldimethylsilyl chloride (*t*BDMSCl), 38%; *c*) adipic acid, DMAP, *N,N'*-dicyclohexylcarbodiimide (DCC), DMF, chloroform ($CHCl_3$), 62%; *d*) tetra-*n*-butylammonium fluoride (TBAF), dichloromethane (DCM), 67%.



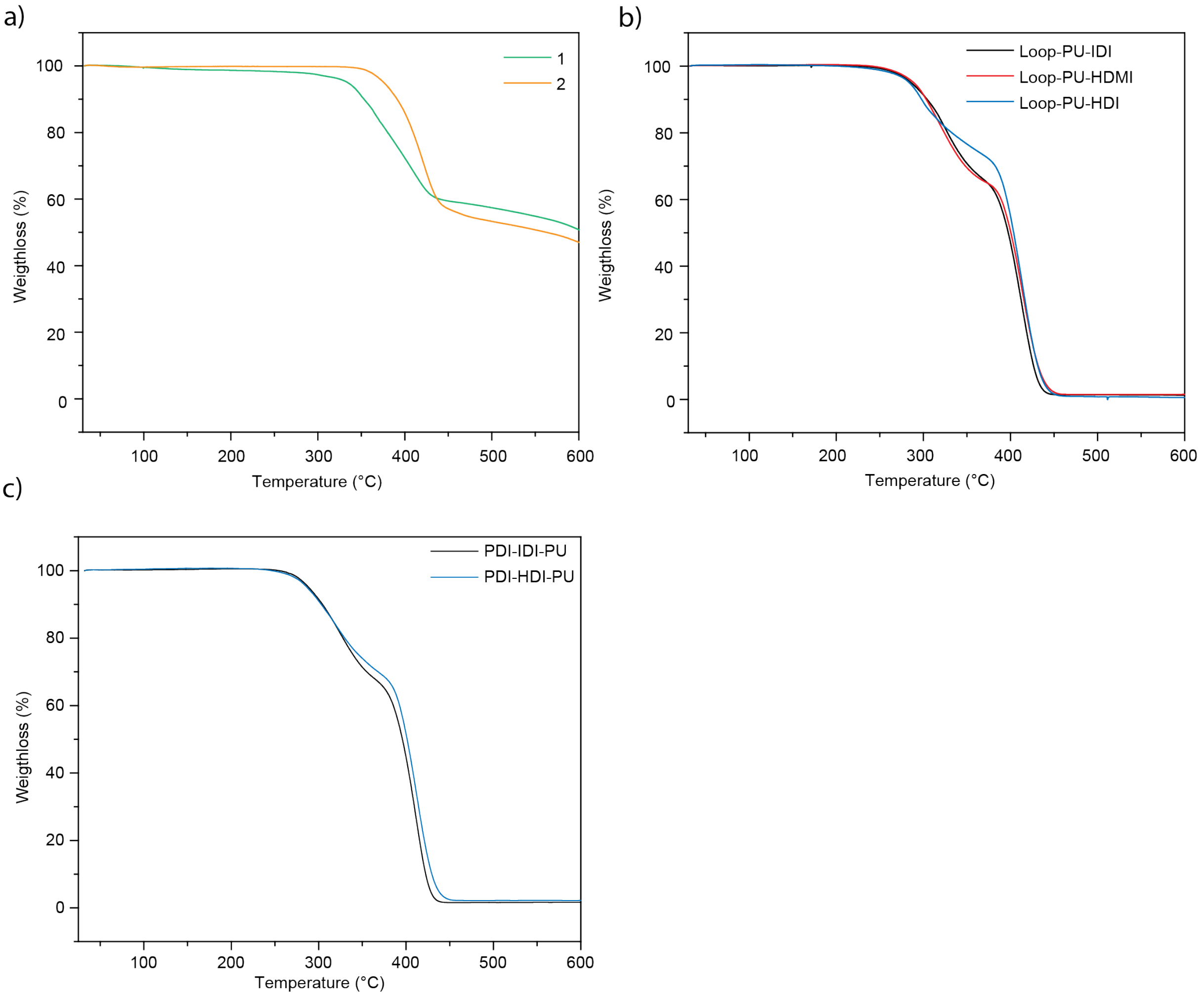
Supplementary Figure S2. Size exclusion chromatography (SEC) traces of (*a*) **Loop-IDI-PU**, (*b*) **Loop-HMDI-PU**, (*c*) **PDI-IDI-PU**, (*d*) **Loop-MDI-PU I**, and (*e*) **Loop-MDI-PU II** (containing 0.03 and 0.12 wt% of **2**, respectively, based on the feed composition) with the refractive index difference (dRI, black trace) and the UV detector signal (red trace). The insets show the number-average molecular weight (M_n) and the dispersity ($Đ$) that were determined against a polystyrene standard calibration.



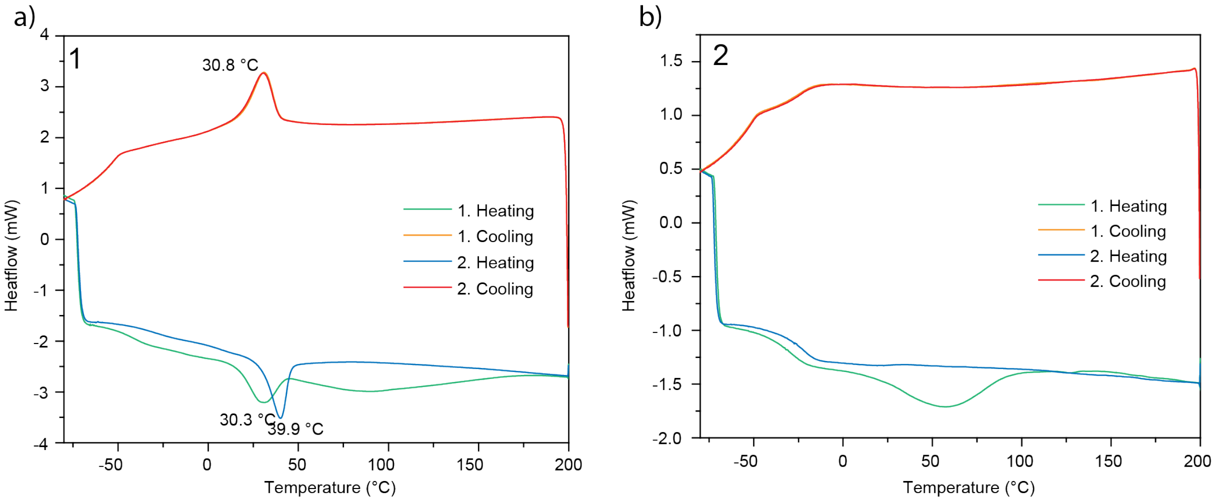
Supplementary Figure S3. (*a*) UV-vis absorption (normalized to the absorbance at 525 nm) and (*b*) fluorescence emission spectra (λ_{ex} = 488 nm, normalized to the emission intensity at 535 nm) of DCM solutions of **PDI-IDI-PU** (c(**1**) = 7 μg mL^{-1}) with photographs of the cuvette (insets) recorded under ambient and UV-light (λ_{ex} = 365 nm), respectively. (*c*) UV-vis absorption spectra of compression-molded films of **PDI-IDI-PU** and **PDI-HDI-PU** with photographs of the films (inset). (*d*) Fluorescence emission spectra (λ_{ex} = 488 nm) of compression-molded films of **PDI-IDI-PU** and **PDI-HDI-PU** (normalized to the emission intensity at 630 nm) and photograph of the films recorded under UV-light illumination (λ_{ex} = 365 nm).



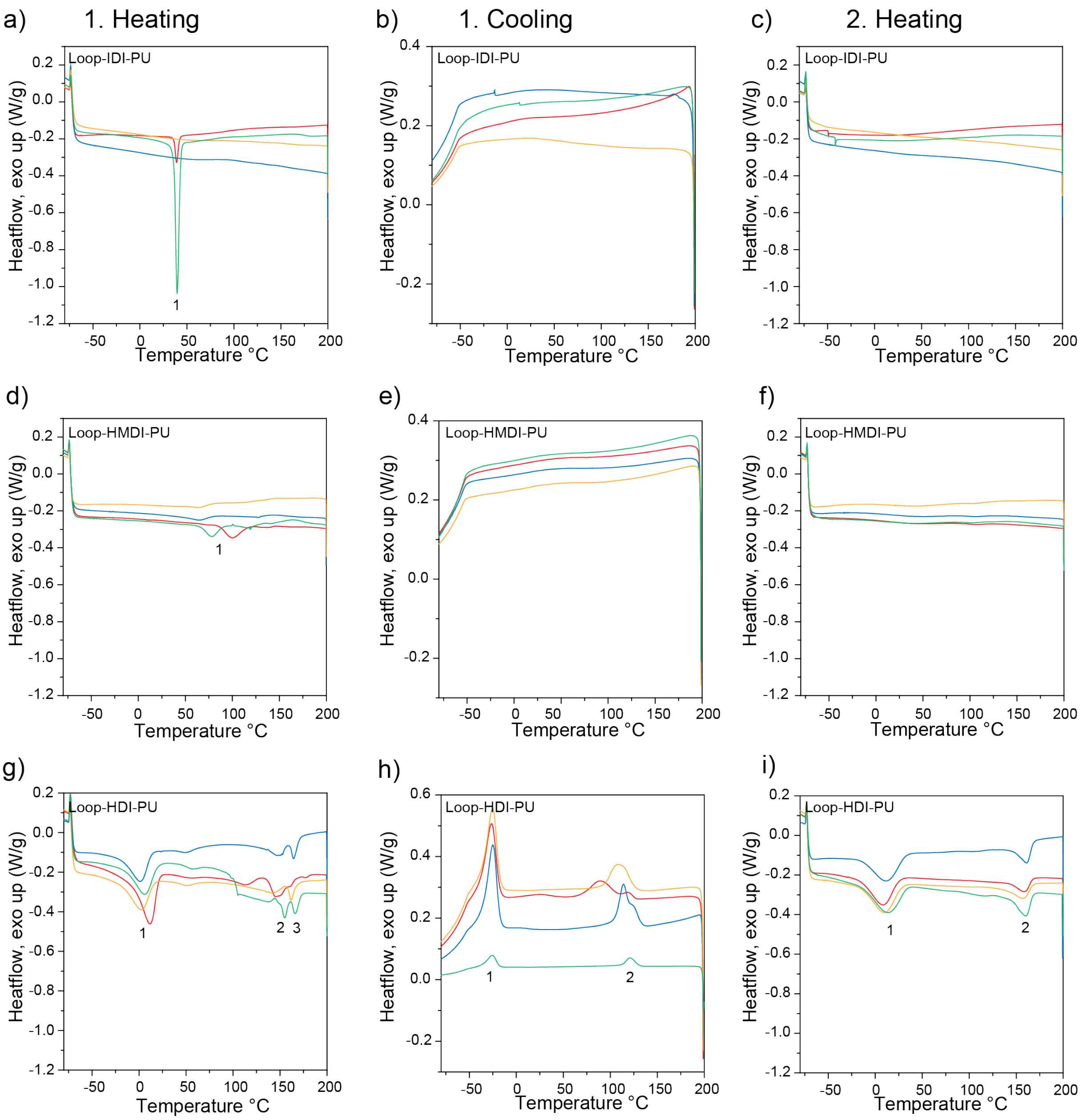
Supplementary Figure S4. (*a*) UV-vis absorption spectra of THF solutions (c = 7 μg ml^{-1} of **2**) of **Loop-MDI-PU I** and **II** (containing 0.03 and 0.12 wt% of **2**, respectively, based on the feed composition) normalized to $I_{525\mathrm{nm}}$ and photograph of the cuvettes (inset). (*b*) Fluorescence emission spectra (λ_{ex} = 488 nm) of THF solutions of **Loop-MDI-PU** 0.03 and 0.12 wt% (c = 7 μg ml^{-1} of **2**) normalized to the emission intensity at 530 nm and photograph of the cuvettes recorded under UV-light illumination (λ_{ex} = 365 nm). (*c*) UV-vis absorption spectra of compression-molded films of **Loop-MDI-PU** containing 0.03 and 0.12 wt% of **2** (based on the feed composition) and photograph of the films (inset). (*d*) Fluorescence emission spectra (λ_{ex} = 488 nm) of compression-molded films of **Loop-MDI-PU** 0.03wt% and 0.12wt% (normalized to the emission intensity at 630 nm) and photograph of the films recorded under UV-light illumination (λ_{ex} = 365 nm).



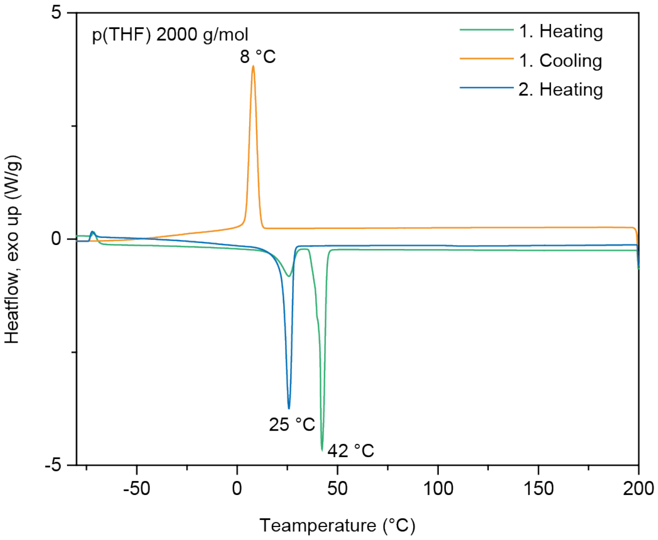
Supplementary Figure S5. Thermogravimetric analysis traces of (*a*) compounds **1** and **2**, (*b*) **Loop-IDI-PU**, **Loop-HDMI-PU**, and **Loop-HDI-PU**, and (*c*) **PDI-IDI-PU** and **PDI-HDI-PU**, all recorded with a heating rate of 10 °C min^{-1}.



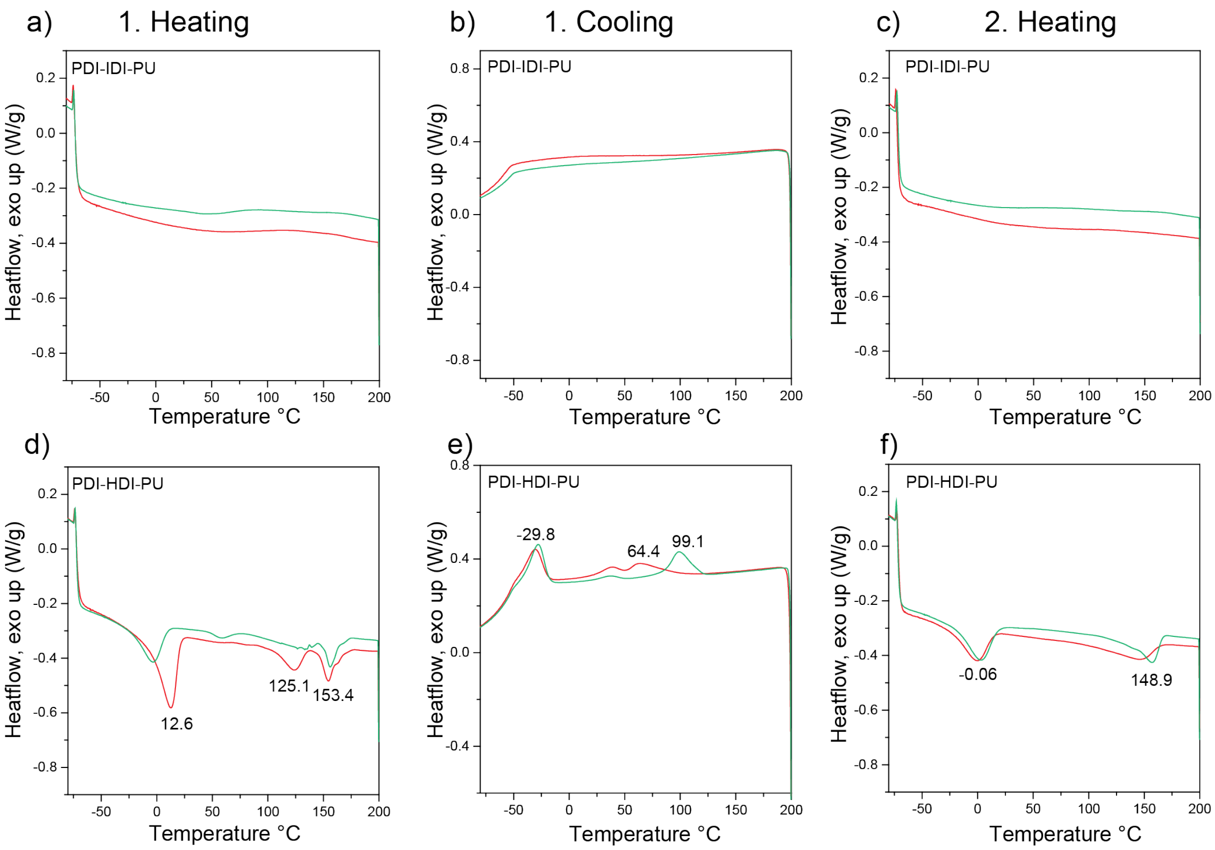
Supplementary Figure S6. Differential scanning calorimetry (DSC) traces of (*a*) **1** and (*b*) **2.** The DSC trace of **1** shows reversible melting and crystallization peaks at 40 and 31 °C, respectively, while the thermogram of **2** shows now characteristic features.



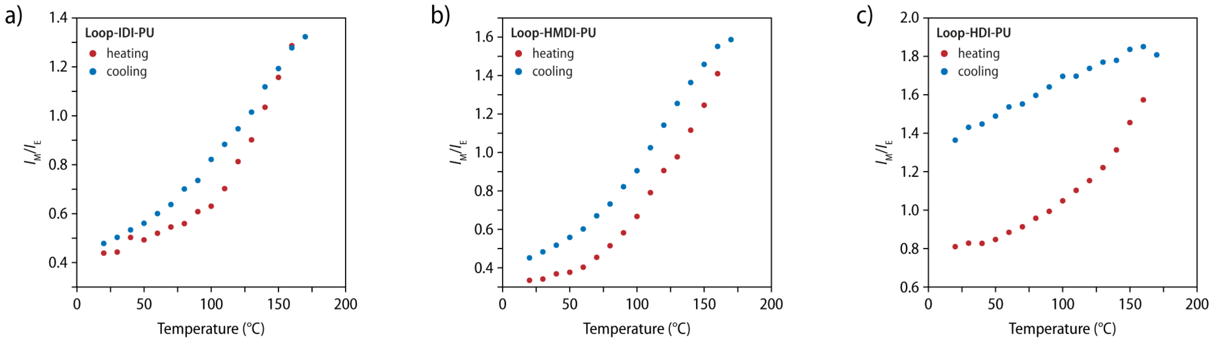
Supplementary Figure S7. Differential scanning calorimetry (DSC) traces of (*a–c*) **Loop-IDI-PU**, (*d–f*) **Loop-HMDI-PU**, and (*g–i*) **Loop-HDI-PU**. Shown are (*a, d, g*) first heating and (*b, e, h*) cooling traces as well as (*c, f, i*) second heating traces. The influence of the processing history was investigated by comparing the pristine material after precipitation and drying (red), compression-molded samples that were cooled rapidly within 5 min (blue) or slowly over the course of 1.5 h (yellow), and compression-molded and slowly cooled samples that were stored under ambient conditions for 5 months (green). **Loop-IDI-PU** shows melting transitions of the p(THF) soft segment in the pristine and the 5-month-old sample at ca. 39 °C, which is not reversible after the first heating. **Loop-PU-HDMI** shows melting of the hard segment in pristine and 5-month-old samples at 100 and 78 °C, respectively, which is irreversible after the first heating. **Loop-PU-HDI** shows strong melting transitions for the soft (3–12 °C) and hard (145–167°C) segments, which are reversible over two heating/cooling cycles. An overview of the thermal transitions is provided in Supplementary Table S1.



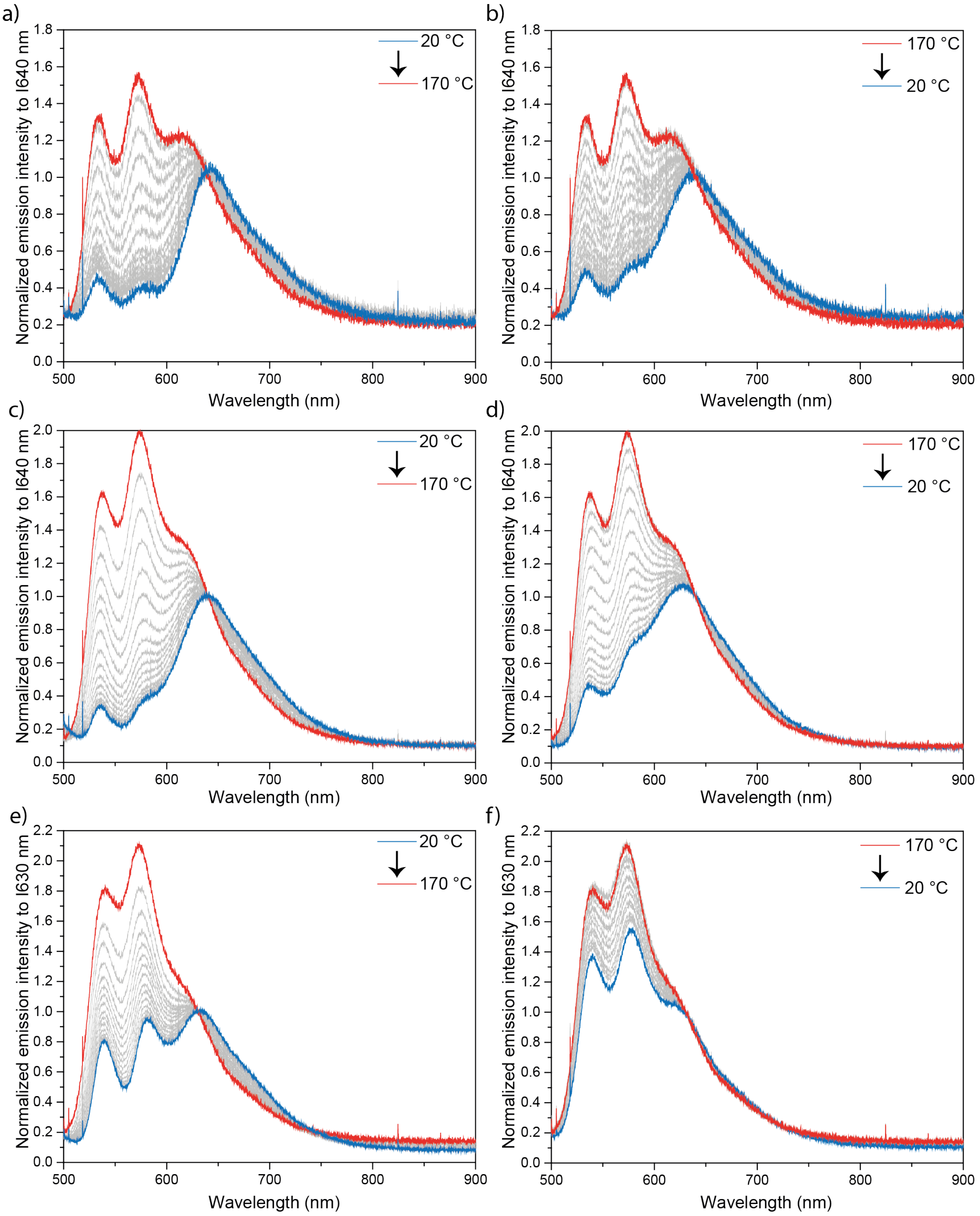
Supplementary Figure S8. Differential scanning calorimetry (DSC) trace of p(THF) (2000 g/mol) that was used as a soft segment in all synthesized polymers. In the first heating cycle melting transitions are seen at 25 °C and 42 °C, while a recrystallization event with maximum at 8 °C is observed in the first cooling cycle. Only one melting transition at 25 °C is observed in the second cooling cycle .



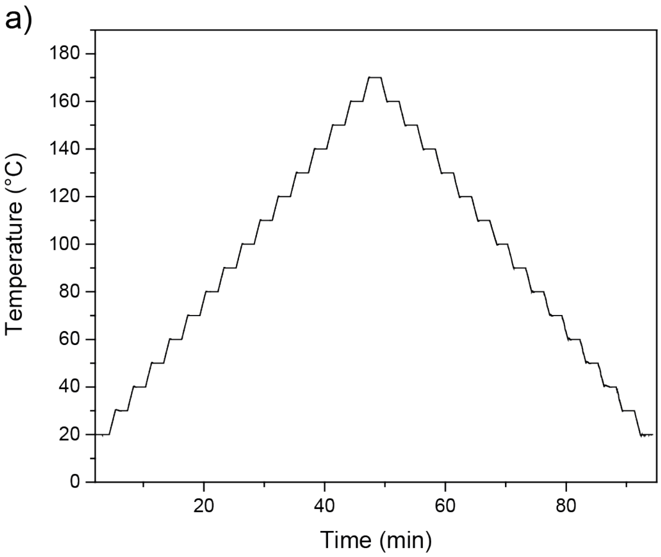
Supplementary Figure S9. Differential scanning calorimetry (DSC) traces of as-prepared precipitated and dried (red) and compression-molded and slowly-cooled three-month-old (green) samples of (*a*–*c*) **PDI-IDI-PU** and (*d*–*e*) **PDI-HDI-PU.** Shown are (*a, d*) first heating and (*b, e*) cooling traces as well as (*c, f*) second heating traces. **PDI-IDI-PU** shows no distinct features, while **PDI-HDI-PU** shows strong melting transitions of soft (0–13 °C) and hard (125–154 °C) segments that are reversible over the two heating/cooling cycles.



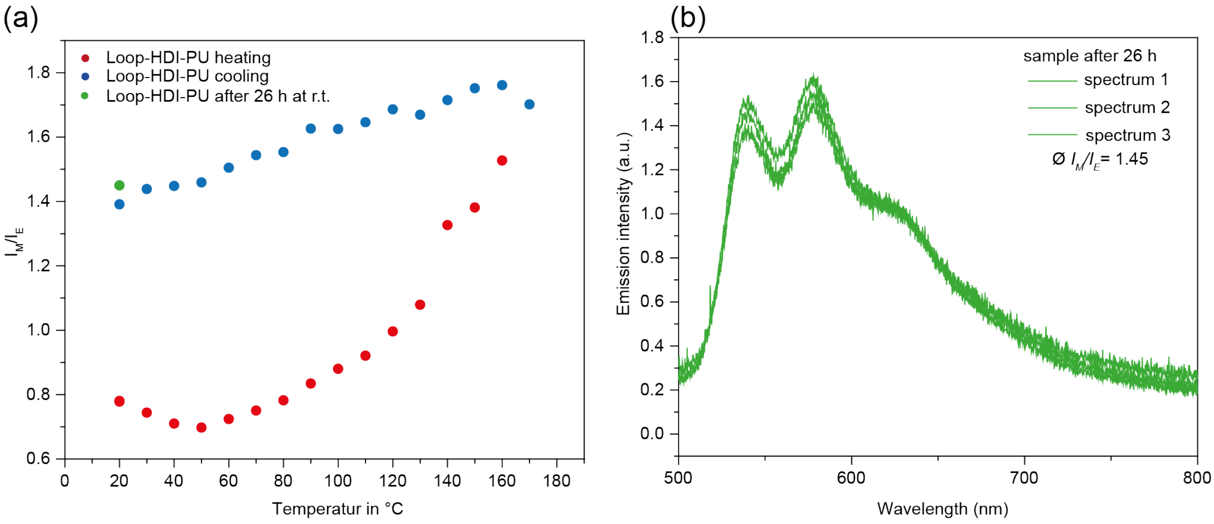
Supplementary Figure S10. Monomer/excimer intensity ratio (IM/IE) as a function of temperature for (a) Loop-IDI-PU, (b) Loop-HMDI-PU, and (c) Loop-HDI-PU recorded upon heating (red circles) and cooling (blue circles). Samples were heated and cooled at rates of 10 °C min−1. The heating/cooling was paused after each 10 °C step, samples were equilibrated for 1 min, and emission spectra (Figure S8) were recorded under excitation at 470 nm. The IM/IE values were determined at 535 and 640 nm for Loop-IDI-PU and Loop-HMDI-PU and at 540 and 630 nm for Loop-HDI-PU.



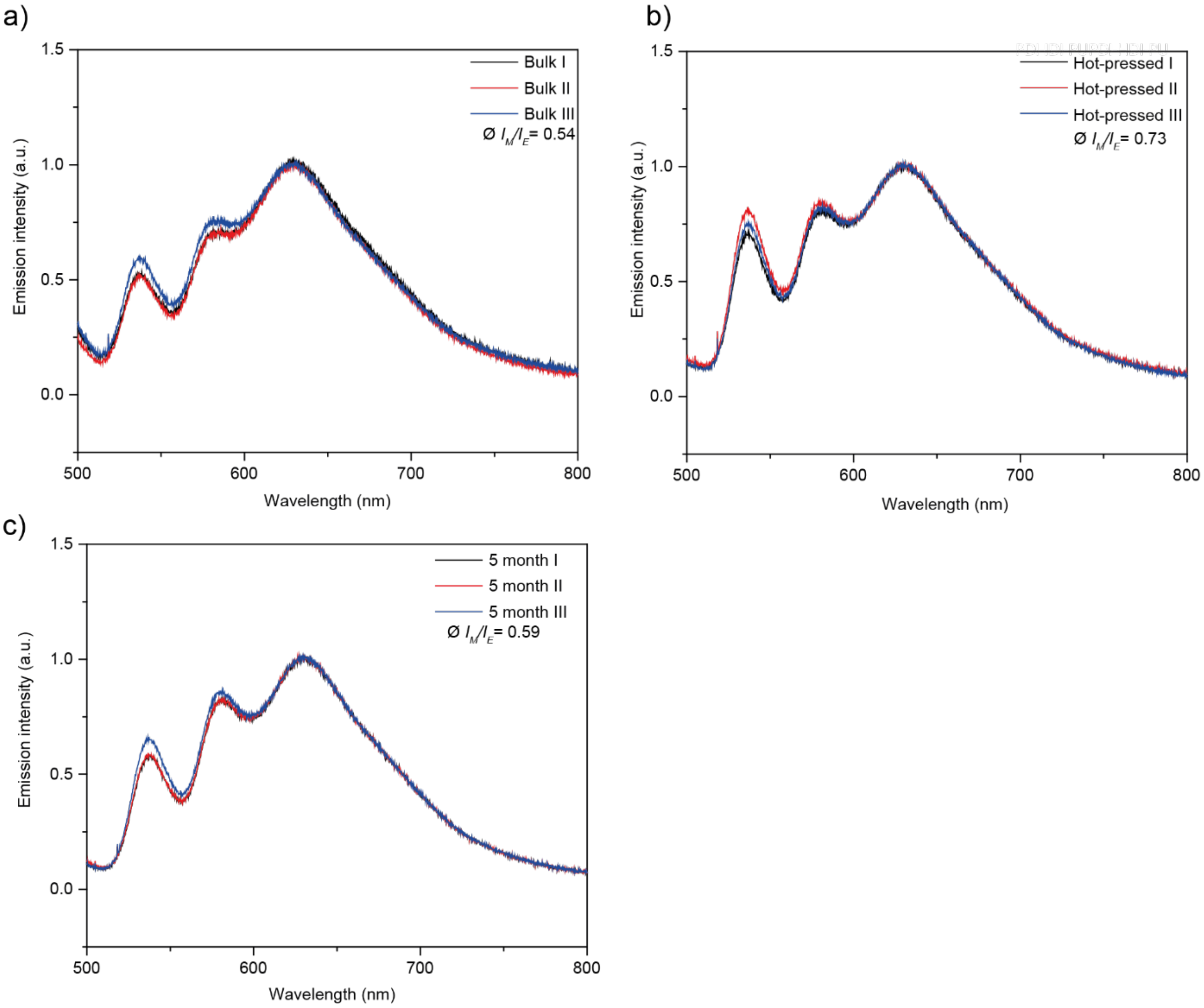
Supplementary Figure S11. Fluorescence emission spectra of compression-molded films of (*a*–*b*) **Loop-IDI-PU**, (*c*–*d*) **Loop-HMDI-PU**, and (*e*–*f*) **Loop-IDI-PU** recorded during heating (*a, c, e*) from 20 to 170 °C and cooling (*b, d, f*) back to 20 °C. Spectra were recorded in steps of 10 °C and the films were equilibrated at each temperature for 1 min before a spectrum was recoded according to the heating and cooling protocol shown in Supplementary Figure S12.



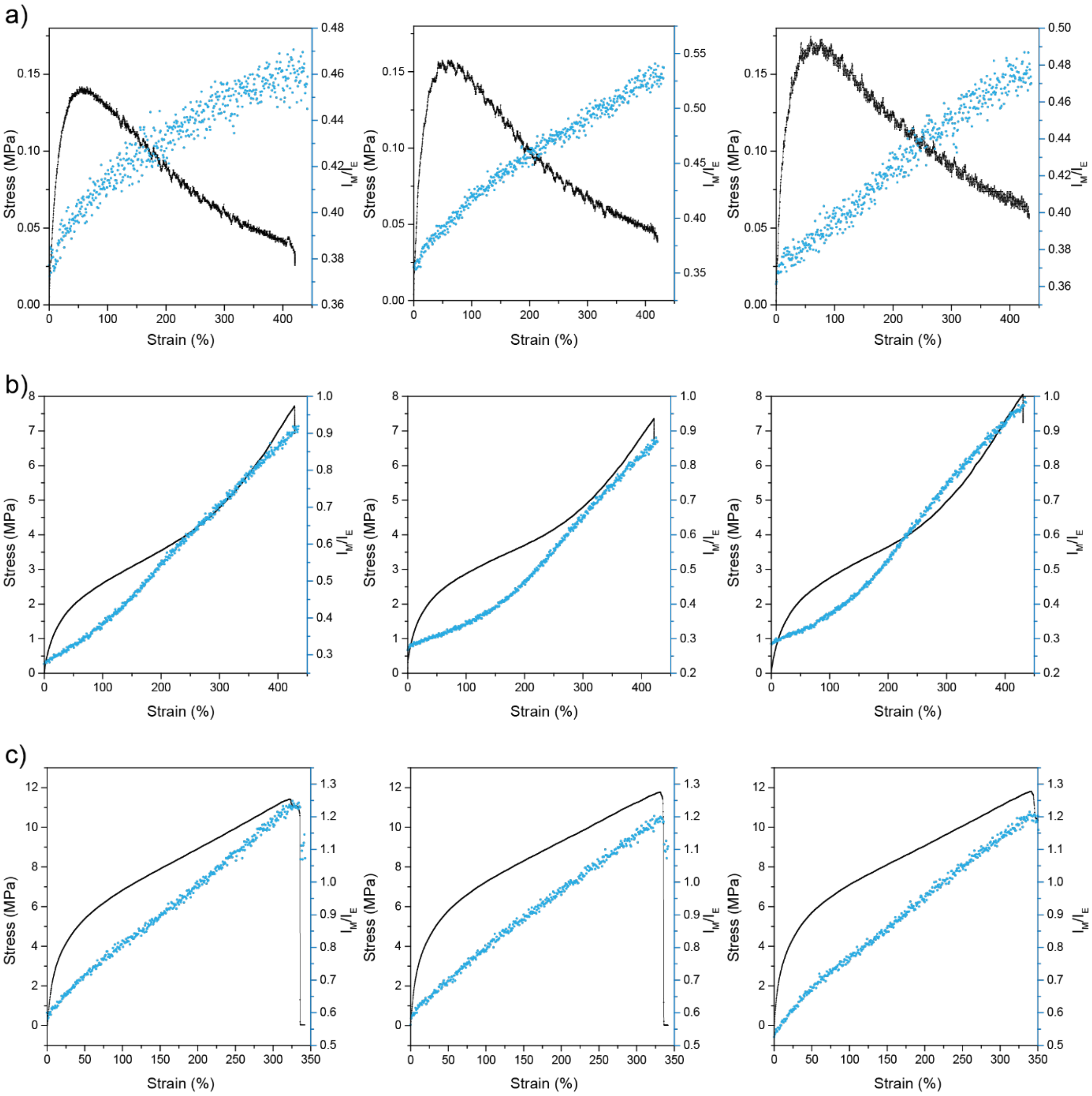
Supplementary Figure S12. Heating and cooling program that was applied to films of **Loop-IDI-PU**, **Loop-HDMI-PU**, and **Loop-HDI-PU** to record the spectra displayed in Figures 4, S11, and S13. The films were kept for 2 min at a given temperature and spectra were recorded after 1 min of equilibration. Afterwards the films were heated with a rate of 10 °C min^{-1} to the next temperature. Spectra were recorded every 10 °C between 20 and 170 °C.



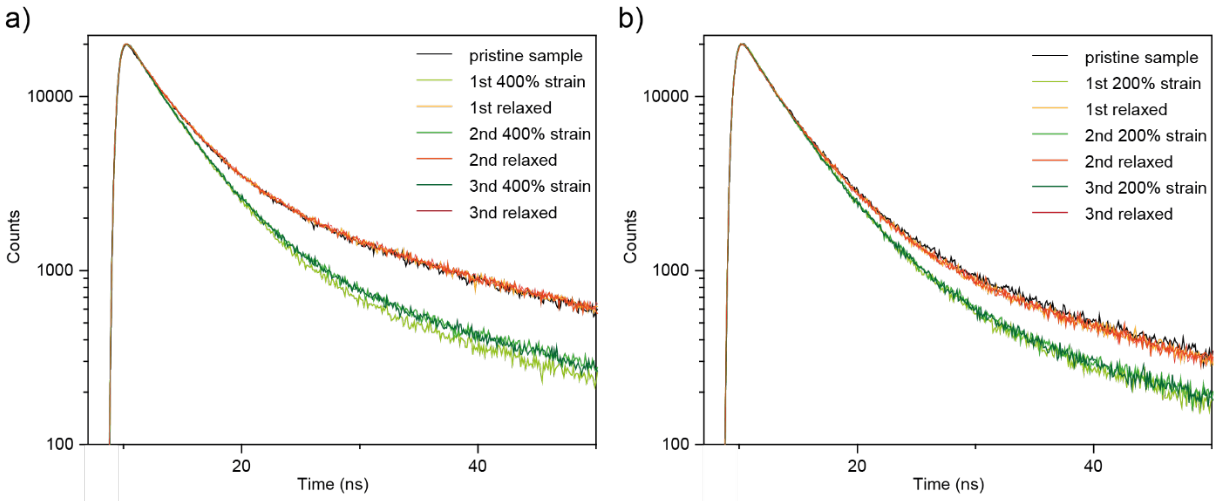
Supplementary Figure S13. (*a*) Monomer/excimer intensity ratio (I_M/I_E) as a function of temperature for **Loop-HDI-PU** recorded upon heating (red circles) and cooling (blue circles) according to the protocol shown in Supplementary Figure S12, and after 26 h at room temperature (green circle). The green data point is the average monomer/excimer ratio of three individual spectra shown in (*b*) that were recorded in different areas of the film. The sample was heated and cooled at a rate of 10 °C min^{-1}. The heating/cooling was paused after each 10 °C step, samples were equilibrated for 1 min, and emission spectra were recorded under excitation at 470 nm. The I_M/I_E values were determined for **Loop-HDI-PU** samples at wavelengths for the monomer of 540 and excimer of 630 nm.



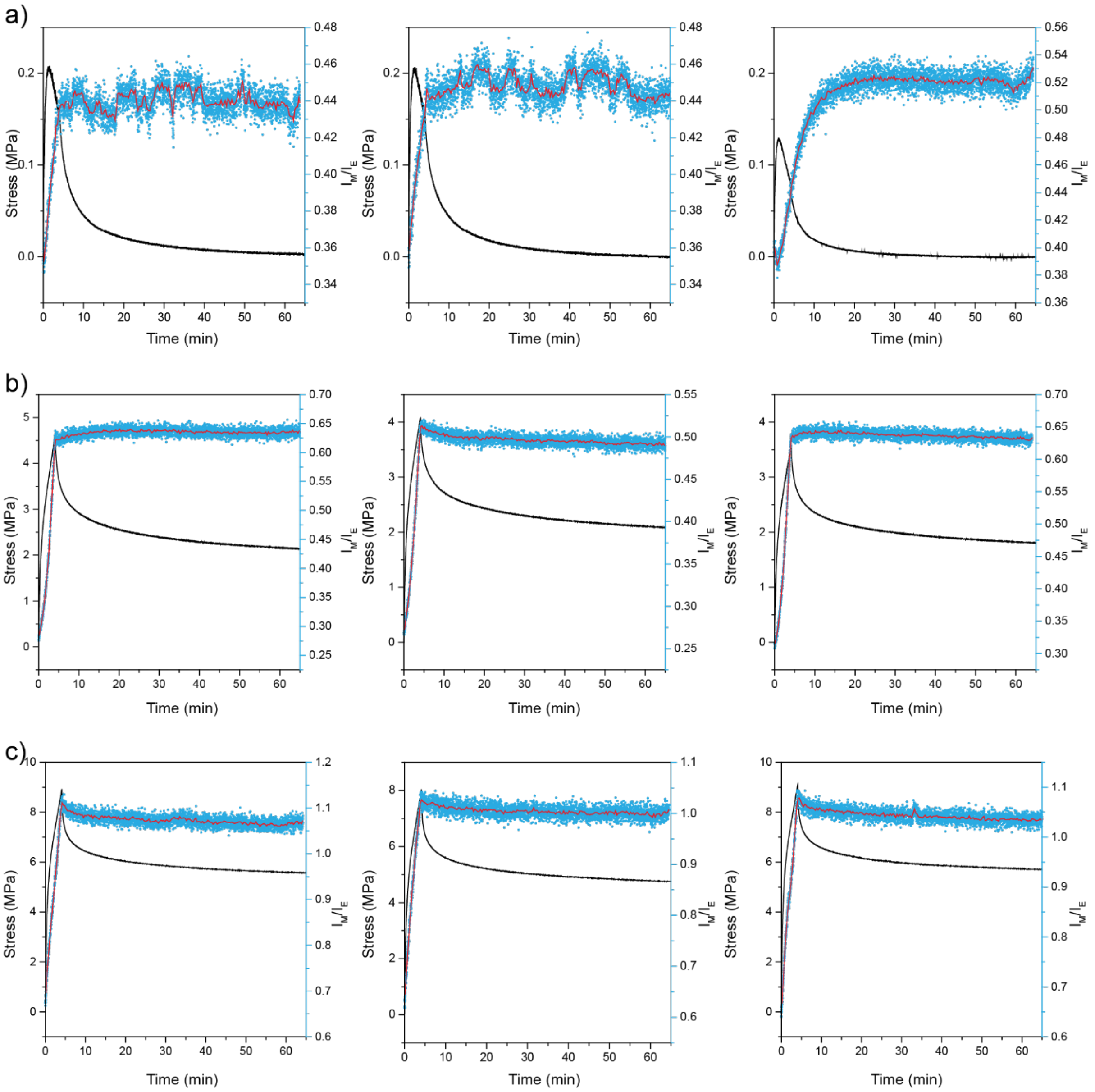
Supplementary Figure S14. Emission spectra of (*a*) the as-prepared samples of **Loop-HDI-PU**, (*b*) a sample of **Loop-HDI-PU** after compression-molding and slow cooling to room temperature, and (*c*) a compression-molded **Loop-HDI-PU** sample that was kept for five months under ambient conditions. Three spectra were recorded on each sample with an excitation wavelength of 470 nm and the average monomer/excimer intensity ratio was calculated (ø I_M/I_E) from the emission intensity at 540 nm for the monomer and at 630 nm for the excimer. All spectra are normalized to the emission intensity at 640 nm.



Supplementary Figure S15. Stress-strain curves (black lines, strain rate 50% min^{-1}) and monomer/excimer intensity ratios (I_M/I_E, blue dots) as a function of applied strain for samples of (*a*) **Loop-IDI-PU**, (*b*) **Loop-HMDI-PU**, and (*c*) **Loop-HDI-PU.** The I_M/I_E ratios were determined from spectra recorded with an excitation wavelength of 470 nm from the emission intensities at 535 and 640 nm for samples of **Loop-IDI-PU** and **Loop-HMDI-PU**, and from the emission intensities at 540 and 630 nm for samples of **Loop-HDI-PU**.



Supplementary Figure S16. Time-resolved fluorescence intensity decays traces recorded over three stretching and relaxation cycles for films of (*a*) **Loop-HMDI-PU** deformed up to 400% strain and (*b*) **Loop-HDI-PU** deformed up to 200% strain. The experiments were carried out with an excitation wavelength of 365 nm and detection at 580 nm.



Supplementary Figure S17. Triplicates of stress relaxation measurements showing the stress (black lines) and the monomer/excimer intensity ratio (I_M/I_E, blue circles) and a 20-point average (red line) recorded over the course of 65 min for samples of (*a*) **Loop-IDI-PU**, (*b*) **Loop-HMDI-PU**, and (*c*) **Loop-HDI-PU**. Films were initially stretched to 200% strain with a strain rate of 50 % min^{-1}. The I_M/I_E ratios were determined for **Loop-IDI-PU** and **Loop-HMDI-PU** samples from the emission intensities at 535 and 640 nm and for **Loop-HDI-PU** samples at 540 and 630 nm. All spectra were recorded with an excitation at 470 nm.

2. Supplementary Tables S1–S2

Supplementary Table S1. Overview of the melting transitions (T_m) and crystallization temperatures (T_c) as determined by differential scanning calorimetry (DSC) of samples of **Loop-IDI-PU**, **Loop-HMDI-PU**, and **Loop-HDI-PU** that were subjected to a varying processing history.

Sample	Pristine material[a] (°C)		Compression-molded[b] Cooled fast (°C)		Compression-molded[b] Cooled slowly (°C)		Stored[c] (°C)	
	T_m	T_c	T_m	T_c	T_m	T_c	T_m	T_c
Loop-IDI-PU	40	–	–	–	–	–	40 °C	–
Loop-HMDI-PU	100	–	–	–	–	–	78 °C	–
Loop-HDI-PU	12 / 145	–25 / 88	4 / 165	–25 / 113	4 / 162	–25 / 109	5 / 155 / 166	–25 / 121
Second heating	9 / 161	–	9 / 161	–	9 / 161	–	9 / 161	–

[a] Polymer samples that were precipitated after the synthesis and dried. [b] Samples that were compression-molded and either cooled fast to room temperature (within 5 min) or slowly cooled to room temperature (over the course of 1.5 h). [c] Compression-molded samples that were slowly cooled and stored under ambient conditions for 5 months.

Supplementary Table S2. Values determined by UV-vis absorption spectroscopy that were used to calculate the extent of association of the perylene dyes[a] for the dye motifs **1** and **2** and for samples of different polyurethanes **Loop-IDI-PU**, **Loop-HMDI-PU**, **Loop-HDI-PU**, **PDI-IDI-PU**, **PDI-HDI-PU**, and **Loop-MDI-PU.**

Sample	A^{0-0} (wavelength)	A^{0-1} (wavelength)	$r = A^{0-0} / A^{0-1}$
1 (in DCM)	0.378 (524 nm)	0.234 (488 nm)	1.62
2 (in DCM)	0.321 (528 nm)	0.387 (491 nm)	0.82
Loop-IDI-PU (in DCM)	0.281 (527 nm)	0.329 (492 nm)	0.85
Loop-HMDI-PU (in DCM)	0.274 (527 nm)	0.323 (492 nm)	0.85
Loop-MDI-PU I (in THF)	0.075 (525 nm)	0.097 (490 nm)	0.77
Loop-MDI-PU II (in THF)	0.124 (525 nm)	0.202 (490 nm)	0.61
PDI-IDI-PU (in DCM)	0.75 (525 nm)	0.431 (488 nm)	1.74
PDI-IDI-PU (film)	0.731 (527 nm)	0.692 (492 nm)	1.06
PDI-HDI-PU (film)	1.119 (527 nm)	0.875 (492 nm)	1.28

[a] Please see the methods section (*vide infra*) for a description of the calculation of the extent of association between the perylene dyes.

3. Captions for Supplementary Movies S1–S3

Supplementary Movie S1. Repeated deformation of a sample of Loop-IDI-PU. A compression-molded film of **Loop-IDI-PU** with dimensions of 20 × 5 × 0.2 mm (length/width/thickness) was manually deformed while held under UV-light illumination (λ_{ex} = 365 nm).

Supplementary Movie S2. Repeated deformation of a sample of Loop-HMDI-PU. A compression-molded film of **Loop-HMDI-PU** with dimensions of 20 × 5 × 0.2 mm (length/width/thickness) was manually deformed while held under UV-light illumination (λ_{ex} = 365 nm).

Supplementary Movie S3. Repeated deformation of a sample of Loop-HDI-PU. A compression-molded film of **Loop-HDI-PU** with dimensions of 20 × 5 × 0.2 mm (length/width/thickness) was manually deformed while held under UV-light illumination (λ_{ex} = 365 nm).

4. Experimental Methods

4.1 Materials and instrumentation

Materials. Perylene-3,4,9,10-tetracarboxylic dianhydride, sodium sulphate, 4-dimethylaminopyridine, dicyclohexylcarbodiimide, adipic acid, tetrabutylammonium fluoride (1.0 M in THF), poly(tetrahydrofuran) (2000 g mol^{-1}), isophorone diisocyanate, dibutyltin dilaurate, hexamethylene diisocyanate, 4,4′-methylene-bis(cyclohexyl isocyanate), 1,4-butanediol, and tert-butyldimethylsilyl chloride were purchased from Sigma Aldrich. 2-(2-(2-(2-Aminoethoxy)ethoxy)ethoxy)ethanol was purchased from ABCR. Sodium chloride was purchased from Reactolab. *N*,*N*-Dimethylformamide, chloroform, and dimethyl sulfoxide were purchased from Acros Organics. Ammonium chloride was purchased from Roth. Dichloromethane, methanol, tetrahydrofuran, and sodium chloride were purchased from either Fisherbrand or Reactolab. Solvents were distilled once prior to use or purchased as spectroscopy grade. Deuterated solvents were purchased from Cambridge Isotope Laboratories. 1,4-Butanediol was distilled once prior to use and poly(tetrahydrofuran) was dried at 60 °C for two days under vacuum prior to use. All other chemicals were used without further purification. If not stated otherwise, reactions were carried out using dried Schlenk glassware under inert gas conditions.

Nuclear magnetic resonance (NMR) spectroscopy. NMR spectroscopy was carried out at 297.2 K on a Bruker Avance DPX 400 spectrometer at frequencies of 400.19 MHz for ^{1}H nuclei and 100.63 MHz for ^{13}C nuclei. Spectra were referenced to the residual solvent peak of $CHCl_3$. Spectra were processed with the MestReNova software suite (v 12.0) 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, m = multiplet, br = broad signal).

Mass spectrometry (MS). Mass spectrometry was performed by the Molecular and Biomolecular Analysis Service (MoBIAS) of ETH Zürich as service measurements. High-resolution matrix-assisted laser desorption ionization (MALDI) mass spectrometry was carried out on a Bruker 9.4T FT-ICR solariX using trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix. High resolution electron spray ionization mass spectrometry was performed on a Bruker maXis-ESI-Qq-TOF-MS.

UV-vis absorption spectroscopy. UV-vis absorption spectra were measured on a Shimadzu UV-2401PC spectrophotometer.

Fluorescence spectroscopy. Steady-state fluorescence spectroscopy in solution or solid state was carried out with a Horiba Fluorolog 3 spectrometer with right angle illumination equipped with a 450 W Xenon light source for excitation and a FL-1030-UP photomultiplier as detector. Fluorescence changes in polymer films as a function of temperature or mechanical strain were recorded using an Ocean Optics USB 4000 spectrometer connected to an Ocean Optics LS-450 LED light source with an excitation wavelength of λ_{ex} = 470 nm and an Ocean Optics QR230-7-XSR SMA 905 optical fibre. Samples were placed on top of a reflective metal block as substrate, the optical fibre was oriented with an angle of 45° relative to the surface at a distance of ca. 2 mm, and the emission spectrum was measured. Spectra were recorded before, after, and during application of mechanical stress and fluorescence data were recorded at an acquisition rate of 1 Hz using the Stream Basic software. Temperature-dependent fluorescence measurements were carried out using a liquid nitrogen-cooled Linkam LS350 heating stage in combination with the Linksys32 software and the Ocean Optics USB 4000 spectrometer as detailed above.

Fluorescence lifetime measurements. Fluorescence lifetime measurements were carried out with a Hamamatsu Photonics Quantaurus-Tau using rectangular-shaped samples with approximate dimensions of 30 × 6 × 0.2 mm (length × width × thickness). The emission decay profiles were recorded for pristine and manually deformed samples with an excitation of 365 nm and detection at 580 nm. The deformation was done manually.

Tensile testing. Stress-strain data were measured on rectangular samples with dimensions of 40 × 5.5 × 0.2 mm (length × width × thickness). The experiments were carried out on a Linkam TST350 micro tensile stage equipped with a 20 N load cell at a strain rate of 50% min^{-1} and Linksys32 software was used to acquire the data. To simultaneously record fluorescence spectra, an Ocean Optics USB 4000 spectrometer as was used as described above.

Differential scanning calorimetry (DSC). DSC measurements were performed on a Mettler Toledo DSC 2 STAR system operated under a nitrogen atmosphere with heating and cooling rates of 10 °C min^{-1} in a temperature range from –80 to 200 °C. Two heating and cooling cycles were measured, and the minimum of the melting peak is reported as the melting temperature T_m, while the maximum of the crystallization peak is reported as the crystallization temperature T_c.

Thermogravimetric analysis (TGA). TGA measurements were performed on a Mettler Toledo TGA/DSC 1 STAR system from 25 to 600°C with a heating rate of 10 °C min^{-1}.

Photographs and videos. Photographs or videos were recorded with a Nikon D7100 digital with an AF-S DX Zoom-NIKKOR 18-135mm lens (f/3.5-5.6G IF-ED) under ambient light or UV-light illumination (λ_{ex} = 365 nm). Photographs were corrected for brightness and contrast.

Flash column chromatography. A Biotage Isolera One flash column chromatography system with a UV-vis detector was used for compound purification.

Microwave reactor. An Initiator 8 EXP Microwave system equipped with an Initiator Robot 8 was used for microwave reactions.

Size exclusion chromatography (SEC). SEC experiments were performed on an Agilent 1200 series HPLC system equipped with an Agilent PLgel mixed guard column (particle size = 5 μm) and two Agilent PLgel mixed-D columns (ID = 7.5 mm, L = 300 mm, particle size = 5 μm). Signals were recorded by a UV detector (Agilent 1200 series), an Optilab REX interferometric refractometer, and a miniDawn TREOS light scattering detector (Wyatt Technology Corp.). Samples were run using THF as the eluent at 30 °C and a flow rate of 1.0 mL min^{-1}. Data analyses were carried out on Astra software (Wyatt Technology Corp.) and molecular weights were determined based on narrow molecular weight poly(styrene) standards.

Preparation of polymer films. Films with a thickness of ca. 200 µm were prepared by compression molding of solvent-cast films of the polymers. Samples were placed in between PTFE sheets in a Carver Inc. press at 80 °C for samples of **Loop-IDI-PU**, 120 °C for samples of **Loop-HMDI-PU**, and at a temperature of 140 °C for samples of **Loop-HDI-PU.** The pressure was increased in steps of 1 ton to prevent bubble formation to a pressure of 4 tons, at which samples were held for 3 min. Afterwards the films were removed from the press and slowly cooled (over the course of 1.5 h) to room temperature between the metal plates. For the DSC experiments described in Supplementary Figure S8 additional samples were prepared as follows: Pristine samples are as-prepared samples after the polymerization reaction that were obtained by precipitation and drying; Compression-molded samples that were cooled fast to room temperature were removed from the metal plates and reached ambient temperature within 5 min; finally, aged samples were obtained after compression-molding and slow cooling samples that were then stored under ambient conditions for 5 months.

Calculation of the degree of folding. The extent of association of the PDI dyes and the folding of the motif **2** into a loop was calculated following a method previously reported by Li and coworkers:[1]

$$r_{\mathrm{obs}} = r_{\mathrm{unfold}} \cdot x_{\mathrm{unfold}} + r_{\mathrm{fold}}(1 - x_{\mathrm{unfold}})$$

$$x_{fold} = 1 - x_{unfold}$$

$$\text{with } r_{\mathrm{obs}} = A_{\mathbf{2}}^{0-0}/A_{\mathbf{2}}^{0-1},\ r_{\mathrm{unfold}} = A_{\mathbf{1}}^{0-0}/A_{\mathbf{1}}^{0-1},\ r_{\mathrm{fold}} = 0.73$$

$$x_{fold\ in\ DCM} = 0.9$$

With r_{obs} determined as the ratio between the intensity values of the relative intensities of the A^{0-0} and A^{0-1} absorption bands of the $S_0 \rightarrow S_1$ vibrational progression of compound **2**. For r_{unfold}, the ratio of the relative intensities of the A^{0-0} and A^{0-1} absorption bands of the $S_0 \rightarrow S_1$ vibrational progression of molecule **1** was considered, assuming that the spectrum of **1** is representative for a non-associated PDI dye. The value for r_{fold} is taken as 0.73, which is the previously reported value for completely associated PDI dyes.[2–4] For the loop-forming motif **2**, the calculation yields a percentage of association of PDI dyes of up to 90%. The ratios calculated in Supplementary Table S2 were calculated from the intensity values of the A^{0-0} and A^{0-1} band maxima from the corresponding UV-vis spectra and calculating the ratio with the following equation.

$$r = A^{0-0}/A^{0-1}$$

4.2 Synthetic procedures

Synthesis of 1. Perylenetetracarboxylic dianhydride (0.4 g, 0.001 mol, 1 eq.) was suspended in dry DMF (20 mL) and 2-(2-(2-(2-aminoethoxy)ethoxy)ethoxy)ethanol (0.394 g, 0.37 mL, 0.002 mol, 2 eq.) was added. The mixture was subjected to 30 min of microwave irradiation at 200 °C. The solvent was removed *in vacuo* and the crude product was purified by flash column chromatography using a gradient elution (DCM to DCM:MeOH 9:1 v/v) to obtain **1** as a dark red solid (0.575 g, 0.7 mmol, 77%).

^{1}H NMR (400 MHz, Chloroform-*d*): δ = 8.45 (d, 4H), 8.29 (d, J = 14.8, 8.1 Hz, 4H), 4.57 – 4.33 (m, 8H), 3.97 – 3.69 (m, 26H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ = 163.8, 134.4, 131.6, 128.9, 125.7, 123.3, 122.4, 70.4, 70.2, 70.1, 69.8, 68.2, 68.2, 66.6, 39.5. HRMS (MALDI): calcd. for $C_{40}H_{42}N_2NaO_{12}$ 765.2630 ([M+Na]$^+$); found: 765.2622.

Synthesis of 2. In a Schlenk flask under nitrogen atmosphere, **4** (0.25 g, 0.15 mmol, 1 eq.) was dissolved in dry DCM (5 mL) and tetrabutylammonium fluoride (1.52 mL, 1 M in THF) was added. The mixture was stirred at ambient temperature overnight, before washing once with saturated aqueous NH_4Cl solution and once with saturated aqueous NaCl solution. The organic phase was isolated, dried over sodium sulphate, and the solvent was removed *in vacuo*. The crude mixture was purified by flash column chromatography (DCM to DCM:MeOH 9:1 v/v) to obtain **2** as a dark red solid (0.160 g, 0.1 mmol; 67%).

^{1}H NMR (400 MHz, Chloroform-d): δ = 8.15 (dd, J = 9.8, 7.9 Hz, 8H), 7.84 (dd, J = 8.3, 3.4 Hz, 7H), 4.38 (q, J = 6.0 Hz, 8H), 4.22 – 4.19 (m, 4H), 3.88 (td, J = 6.0, 3.7 Hz, 8H), 3.80 – 3.75 (m, 8H), 3.73 – 3.55 (m, 37H), 2.38 – 2.29 (m, 4H), 1.65 (h, J = 3.3 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ = 173.4, 162.9, 162.8, 133.5, 133.5, 131.0, 130.8, 130.7, 128.6, 128.5, 125.3, 122.8, 122.6, 72.7, 72.7, 70.9, 70.8, 70.8, 70.7, 70.7, 70.5, 70.3, 70.2, 69.3, 68.1, 68.0, 63.7, 61.9, 39.5, 33.9, 24.5, 1.2. HRMS (ESI): calcd. for $C_{86}H_{90}N_4Na_2O_{26}$ ([M+Na]$^+$); 820.2814 found: 820.2815.

Synthesis of 3. 1 Following a previous protocol by Wang *et al.*,[5] (1.5 g, 2.0 mmol, 1 eq.) was dissolved in pyridine and 4-(dimethylamino)pyridine (0.075 g, 0.6 mmol, 0.3 eq) and *tert*-butyldimethylsilyl chloride (0.7 g, 4.7 mmol, 2.3 eq.) were added. The mixture was stirred overnight followed by removal of the solvent *in vacuo*. The crude mixture was purified by column flash column chromatography using a gradient elution (DCM to DCM:MeOH 9:1 v/v) to obtain **3** as a brown solid (0.66 g, 0.8 mmol, 38%).

^{1}H NMR (400 MHz, Chloroform-*d*): δ = 8.40 (dd, J = 8.0, 2.5 Hz, 4H), 8.20 (dt, J = 8.3, 1.4 Hz, 4H), 4.44 (t, J = 6.0 Hz, 4H), 3.93 – 3.46 (m, 28H), 0.86 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ = 163.2, 163.2, 134.1, 134.1, 131.1, 129.1, 125.9, 123.1, 123.1, 122.9, 72.8, 72.7, 70.8, 70.8, 70.8, 70.5, 70.3, 68.1, 68.0, 62.8, 61.9, 39.5, 39.5, 26.1, 18.5, 1.2, –5.1. HRMS (ESI): calcd. for $C_{46}H_{56}N_2NaO12Si$ ([M+Na]$^+$); 879.3495 found: 879.3485.

Synthesis of 4. Following a previous protocol by Chen *et al.*,[6] **3** (0.55 g, 0.64 mmol, 2 eq.) and 4-(dimethylamino)pyridine (0.078 g, 0.64 mmol, 2 eq.) were added to a Schlenk flask under nitrogen atmosphere and dissolved in dry $CHCl_3$ (10 mL). Adipic acid (0.046 g, 0.3 mmol, 1 eq.) was separately dissolved in dry DMF

(2 mL) and added to the mixture, followed by drop-wise addition of a solution of *N,N′*-dicyclohexylcarbodiimide (0.238 g 1.0 mmol, 3.6 eq.) in dry $CHCl_3$ (2 mL). The mixture was stirred for 48 h and the crude material subjected to flash column chromatography using a gradient elution (DCM to DCM:MeOH 9:1 v/v) to obtain **4** as a dark red powder (0.329 g, 0.2 mmol, 63%).

^{1}H NMR (400 MHz, Chloroform-d): δ = 8.27 (dd, *J* = 15.8, 7.9 Hz, 8H), 8.01 (dd, *J* = 8.2, 6.6 Hz, 7H), 4.42 (q, *J* = 6.2 Hz, 8H), 4.23 – 4.15 (m, 4H), 3.88 (td, *J* = 6.0, 3.1 Hz, 8H), 3.82 – 3.57 (m, 38H), 3.51 (t, *J* = 5.5 Hz, 4H), 2.41 – 2.25 (m, 4H), 1.67 – 1.59 (m, 4H), 0.86 (s, 18H), 0.03 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ = 173.4, 163.0, 163.0, 133.8, 130.9, 130.9, 128.8, 128.8, 125.6, 125.6, 123.0, 122.9, 122.7, 122.7, 72.8, 72.7, 70.9, 70.8, 70.8, 70.8, 70.8, 70.7, 70.3, 70.2, 69.3, 68.1, 68.0, 63.6, 62.8, 39.5, 33.9, 26.1, 24.5, 18.5, 1.2, –5.1. HRMS (ESI): calcd. for $C_{98}H_{118}N_4Na_3O_{26}Si_2$ ([M+Na]$^+$); 630.5750 found: 630.5744.

Synthesis of Loop-IDI-PU. Poly(tetrahydrofuran) (2000 g mol^{-1}, 3.00 g, 1.5 mmol) was dried under vacuum at 60 °C over the course of two days and added to an oven-dried Schenk flask equipped with a magnetic stirring bar. Isophorone diisocyanate (1.06 mL, 1.12 g, 5.0 mmol) and **2** (0.003 g, 1.9 µmol) were added and the mixture was dissolved in dry $CHCl_3$ (15 mL). Two drops of dibutyltin dilaurate were added. After stirring the mixture for 3 h at 45 °C, freshly distilled 1,4-butanediol (0.3 g, 0.294 mL, 3.3 mmol) was added, and stirring was continued for 48 h at 45 °C. When the solution turned too viscous to be stirred by the magnetic stirring bar, dry THF (15 mL) was added. The reaction was eventually quenched by addition of 5 mL MeOH, the mixture was precipitated into cold hexane, and the polymer was collected by filtration. After drying under vacuum at 70 °C, **Loop-IDI-PU** was obtained as a dark red rubbery solid (4.1 g, 93 %).

^{1}H NMR (300 MHz, Chloroform-*d*): δ = 5.06 – 4.40 (m, 1H), 4.22 – 3.92 (m, 2H), 3.72 (d, *J* = 36.2 Hz, 1H), 3.40 (tq, *J* = 5.1, 2.4, 1.7 Hz, 14H), 2.90 (d, *J* = 6.7 Hz, 1H), 1.95 – 0.74 (m, 24H). SEC (THF, PS standard) M_n: 31800 g mol^{-1}, M_w: 57750 g mol^{-1}, $Đ$: 1.8.

Synthesis of Loop-HMDI-PU. Poly(tetrahydrofuran) (2000 g mol^{-1}, 3.00 g, 1.5 mmol) was dried under vacuum at 60°C over two days and added to an oven-dried Schenk flask equipped with a magnetic stirring bar. 4,4′-Methylenebis(cyclohexyl isocyanate) (isomer mixture; 1.24 mL, 1.33 g, 5.0 mmol) and **2** (0.003 g, 1.9 µmol) were added and the mixture was dissolved in dry $CHCl_3$ (15 mL). Two drops of dibutyltin dilaurate were added, the mixture was stirred for 3 h at 45 °C, 1,4-butanediol (0.3 g, 0.294 mL, 3.3 mmol) was added, and stirring was continued for 48 h at 45 °C. When the solution turned too viscous to be stirred by the magnetic stirring bar, dry THF (15 mL) was added. The reaction was eventually quenched by addition of 5 mL MeOH, the mixture was precipitated into cold hexane, and the polymer was collected by filtration. After drying under vacuum at 70 °C, **Loop-HMDI-PU** was obtained as a pink rubbery solid (4.3 g, 93%).

^{1}H NMR (400 MHz, Chloroform-*d*): δ = 4.79 (s, 1H), 4.51 (s, 1H), 4.06 (d, *J* = 6.7 Hz, 6H), 3.71 (d, *J* = 42.8 Hz, 2H), 3.41 (h, *J* = 3.4 Hz, 42H), 2.06 – 1.90 (m, 3H), 1.83 – 0.73 (m, 73H). SEC (THF, PS standard) M_n: 31230 g mol^{-1} M_w: 65760 g mol^{-1}, Đ: 2.1.

Synthesis of Loop-HDI-PU. Poly(tetrahydrofuran) (2000 g mol^{-1}, 3.00 g, 1.5 mmol) was dried under vacuum at 60°C over two days and added to an oven-dried Schenk flask equipped with a magnetic stirring bar. Hexamethylene diisocyanate (0.803 mL, 0.841 g, 0.005 mol) and **2** (0.003 g, 0.0019 mmol) were added and the mixture was dissolved in dry $CHCl_3$ (15 mL). Two drops of dibutyltin dilaurate were added, the mixture was stirred for 3 h at 45 °C, 1,4-butanediol (0.3 g, 0.294 mL, 3.3 mmol) was added, and stirring was continued for 48 h at 45 °C. When the solution turned too viscous to be stirred by the magnetic stirring bar, dry THF (15 mL) was added. The reaction was eventually quenched by addition of 5 mL MeOH, the mixture was precipitated into cold hexane, and the polymer was collected by filtration. After drying under vacuum at 70 °C, **Loop-HDI-PU** was obtained as a pink rubbery solid (4.0 g, 96%).

^{1}H NMR (400 MHz, Chloroform-*d*): δ = 4.16 (q, *J* = 4.7, 3.7 Hz, 1H), 3.64 (q, *J* = 5.6, 4.9 Hz, 6H), 3.24 – 3.07 (m, 1H), 1.88 – 1.12 (m, 11H).

Synthesis of Loop-MDI-PU 0.03wt%. Poly(tetrahydrofuran) (2000 g mol^{-1}, 1.50 g, 0.75 mmol) was dried under vacuum at 60°C over two days and added to an oven-dried Schenk flask equipped with a magnetic stirring bar. 4,4′-Methylenebis(phenylisocyanate) (0.63 g, 2.5 mmol) and **2** (0.6 mg, 0.7 µmol) were added and the mixture was dissolved in dry THF (8 mL) and dry $CHCl_3$ (12.5 mL). Two drops of dibutyltin dilaurate were added, the mixture was stirred for 3 h at room temperature, freshly distilled 1,4-butanediol (0.15 g, 0.0017 mol) was added, and stirring was continued for 48 h. The reaction was eventually quenched by addition of 5 mL MeOH, the mixture was precipitated into cold hexane, and the polymer was collected by filtration. After drying under vacuum at 70 °C, **Loop-MDI-PU I** was obtained as a pink rubbery solid. Yield not determined.

^{1}H NMR (400 MHz, THF-*d*$_8$) δ 8.57 (s, 1H), 7.36 (dd, *J* = 8.6, 2.4 Hz, 3H), 7.03 (d, *J* = 8.3 Hz, 3H), 4.11 (d, *J* = 13.1 Hz, 2H), 3.82 (s, 2H), 3.37 (dt, *J* = 5.9, 3.4 Hz, 30H), 1.85 – 1.68 (m, 15H), 1.58 (p, *J* = 3.0 Hz, 29H). SEC (THF, PS standard) M_n: 84’910 g mol^{-1}, M_w: 147’300 g mol^{-1}, *Đ*: 1.7.

Synthesis of Loop-MDI-PU 0.12wt%. Poly(tetrahydrofuran) (2000 g mol^{-1}, 1.50 g, 0.75 mmol) was dried under vacuum at 60°C over two days and added to an oven-dried Schenk flask equipped with a magnetic stirring bar. 4,4′-Methylenebis(phenylisocyanate) (0.63 g, 2. 5 mmol) and **2** (2.7 mg, 3.4 µmol) were added and the mixture was dissolved in dry THF (8 mL) and dry $CHCl_3$ (12.5 mL). Two drops of dibutyltin dilaurate were added, the mixture was stirred for 3 h at room temperature, freshly distilled 1,4-butanediol (0.15 g, 0.0017 mol) was added, and stirring was continued for 48 h. The reaction was eventually quenched by addition of 5 mL MeOH, the mixture was precipitated into cold hexane, and the polymer was collected by filtration. After drying under vacuum at 70 °C, **Loop-MDI-PU II** was obtained as a dark red rubbery solid. Yield not determined.

^{1}H NMR (400 MHz, THF-*d*$_8$) δ 8.57 (s, 1H), 7.36 (dd, *J* = 8.6, 2.5 Hz, 3H), 7.03 (d, *J* = 8.2 Hz, 4H), 4.19 – 4.04 (m, 3H), 3.82 (s, 2H), 3.37 (dt, *J* = 5.9, 3.2 Hz, 28H), 1.82 – 1.69 (m, 12H), 1.65 – 1.47 (m, 27H). SEC (THF, PS standard) M_n: 58’310 g mol^{-1}, M_w: 112’200 g mol^{-1}, *Đ*: 1.9.

Synthesis of PDI-IDI-PU. Poly(tetrahydrofuran) (2000 g mol^{-1}, 3.00 g, 1.5 mmol) was dried under vacuum at 60°C over two days and added to an oven-dried Schenk flask equipped with a magnetic stirring bar. Isophorone diisocyanate (1.06 mL, 1.12 g, 5.0 mmol) and **1** (0.00214 g, 2.9 µmol) were added and the mixture was dissolved in dry $CHCl_3$ (15 mL). Two drops of dibutyltin dilaurate were added, the mixture was stirred for 3 h at 45 °C, freshly distilled 1,4-butanediol (0.3 g, 0.294 mL, 3.3 mmol) was added, and stirring was continued for 48 h at 45 °C. When the solution turned too viscous to be stirred by the magnetic stirring bar, dry THF (15 mL) was added. The reaction was eventually quenched by addition of 5 mL MeOH, the mixture was precipitated into cold hexane, and the polymer was collected by filtration. After drying under vacuum at 70 °C, **PDI-IDI-PU** was obtained as a red rubbery solid (3.85 g, 87%).

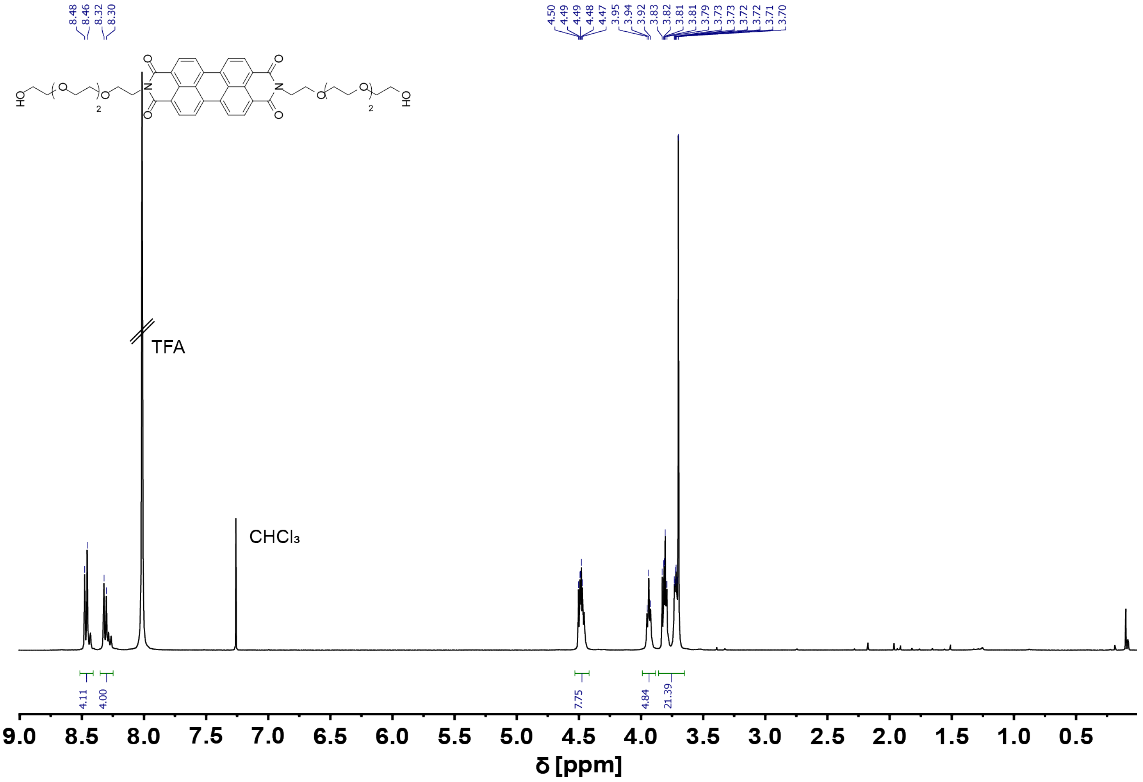
^{1}H NMR (400 MHz, Chloroform-*d*): δ = 4.67 (d, J = 108.0 Hz, 1H), 4.19 – 3.90 (m, 2H), 3.79 (d, J = 10.1 Hz, 1H), 3.40 (tq, J = 4.9, 2.5, 1.7 Hz, 19H), 2.90 (d, J = 6.8 Hz, 1H), 1.97 – 1.50 (m, 20H), 1.30 – 0.67 (m, 6H). SEC (THF, PS standard) M_n: 132’600 g mol^{-1}, M_w: 221’400 g mol^{-1}, Đ: 1.7.

Synthesis of PDI-HDI-PU. Poly(tetrahydrofuran) (2000 g mol^{-1}, 3.00 g, 1.5 mmol) was dried under vacuum at 60°C over two days and added to an oven-dried Schenk flask equipped with a magnetic stirring bar. Hexamethylene diisocyanate (0.803 mL, 0.841 g, 5.0 mol) and **1** (2.14 mg, 2.9 µmol) were added and the mixture was dissolved in dry $CHCl_3$ (15 mL). Two drops of dibutyltin dilaurate were added, the mixture was stirred for 3 h at 45 °C, freshly distilled 1,4-butanediol (0.3 g, 0.294 mL, 3.3 mmol) was added, and stirring was continued for 48 h at 45 °C. When the solution turned too viscous to be stirred by the magnetic stirring bar, dry THF (15 mL) was added. The reaction was eventually quenched by addition of 5 mL MeOH, the mixture was precipitated into cold hexane, and the polymer was collected by filtration. After drying under vacuum at 70 °C, **PDI-HDI-PU** was obtained as an orange rubbery solid (3.86 g, 93 %).

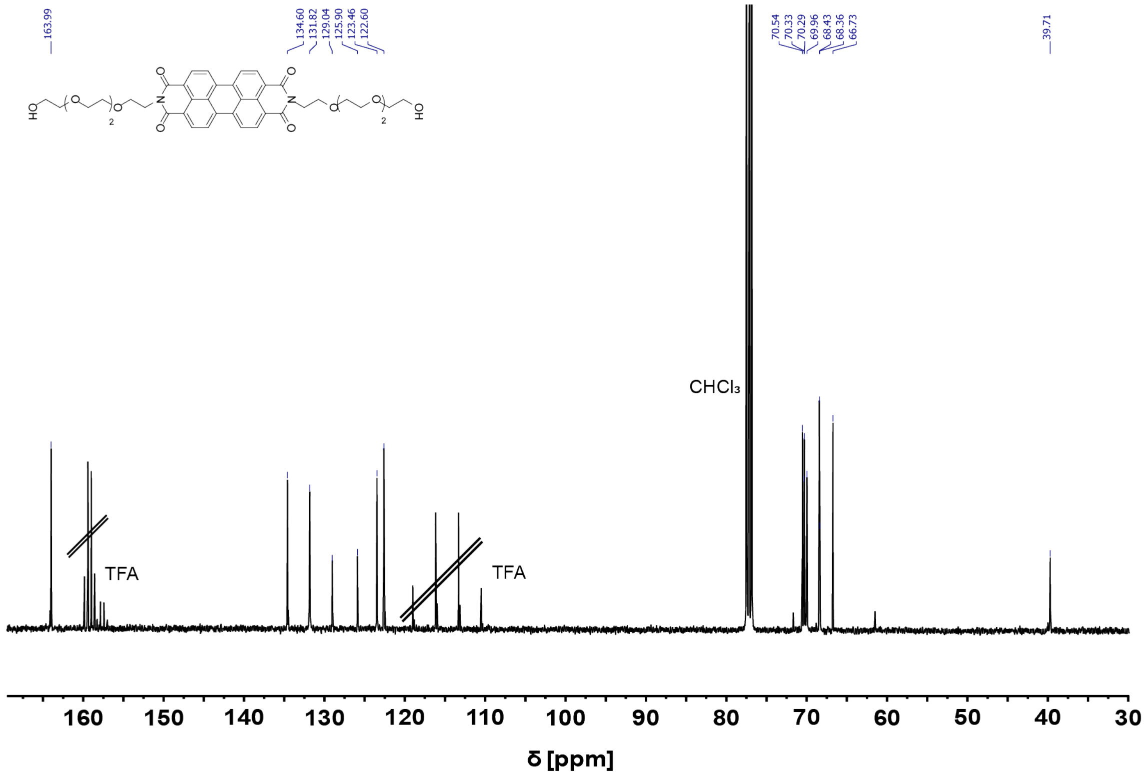
^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.21 (s, 1H), 5.04 (s, 1H), 4.09 (s, 4H), 3.66 – 3.29 (m, 34H), 3.15 (s, 6H), 1.90 – 0.99 (m, 51H).

5. NMR Spectra

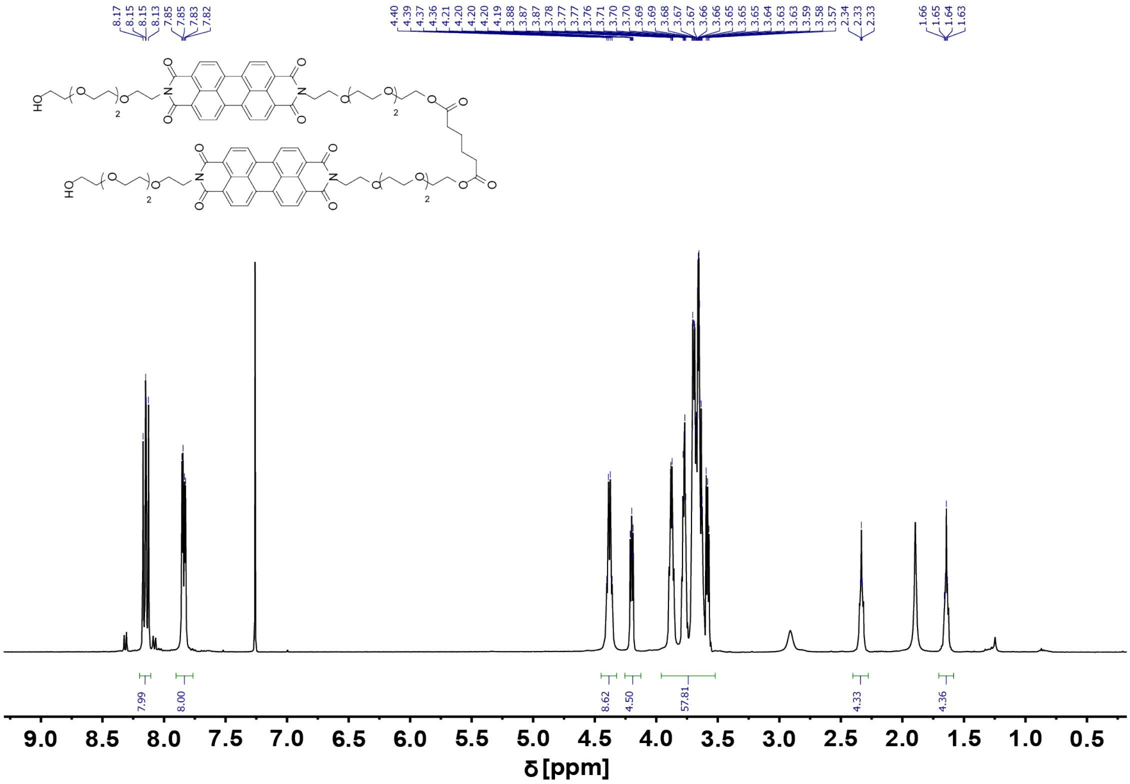
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1**.



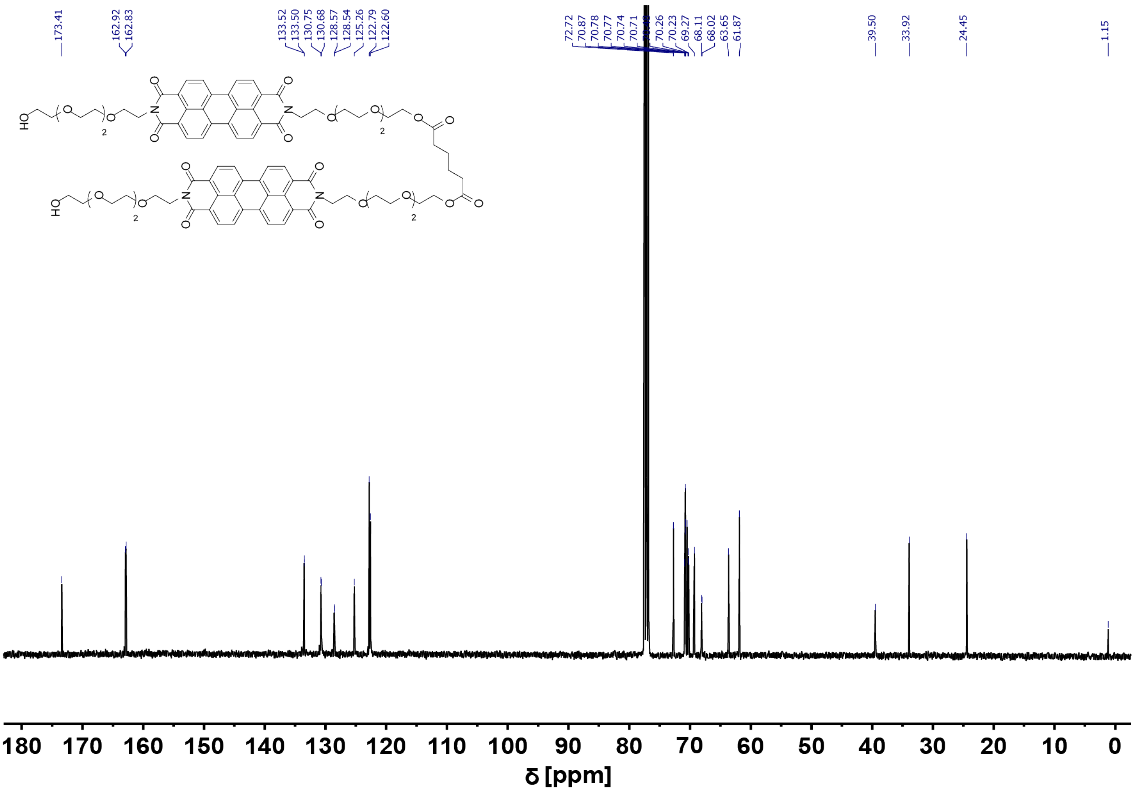
^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **1**.



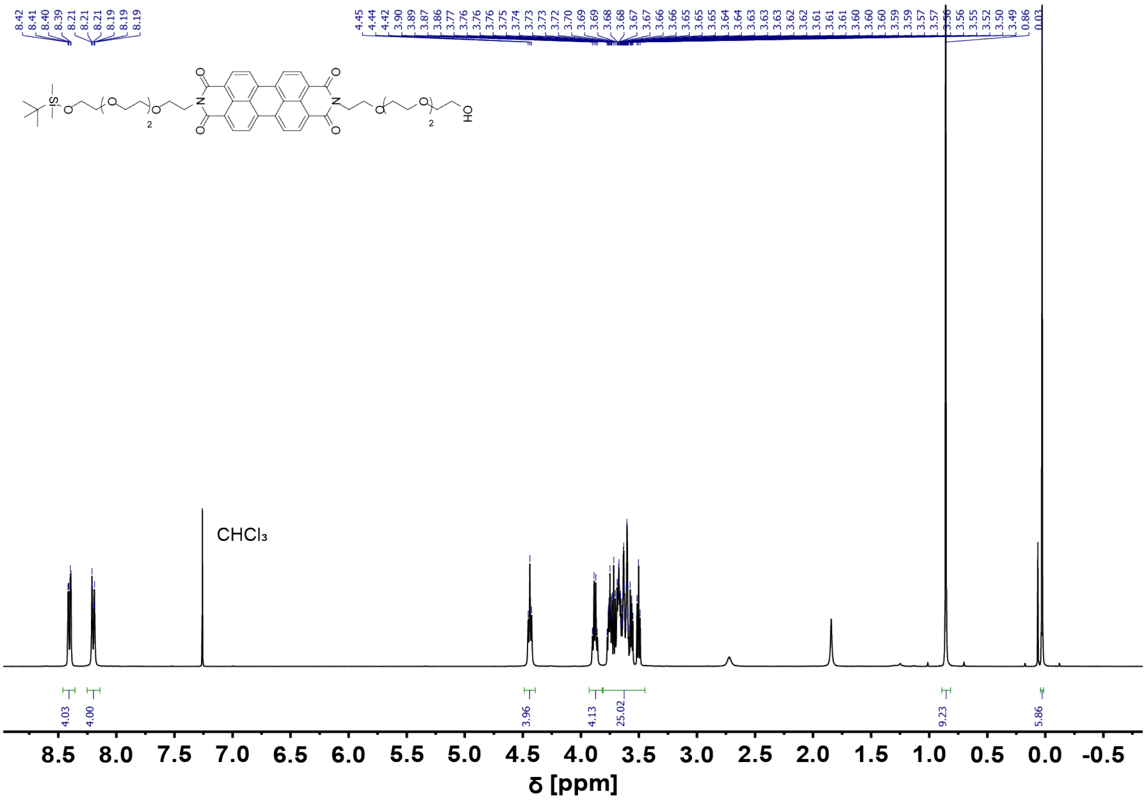
^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of **2**.



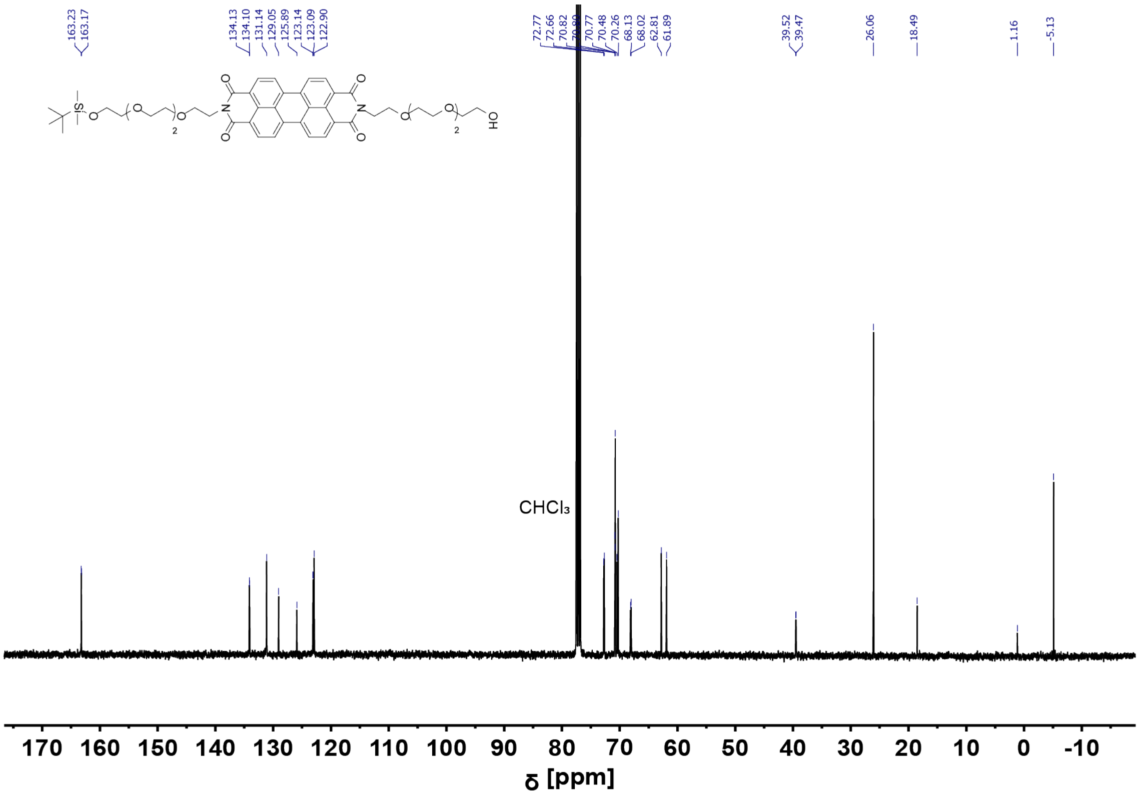
^{13}C NMR spectrum (CDCl$_3$, 101 MHz) of **2**.



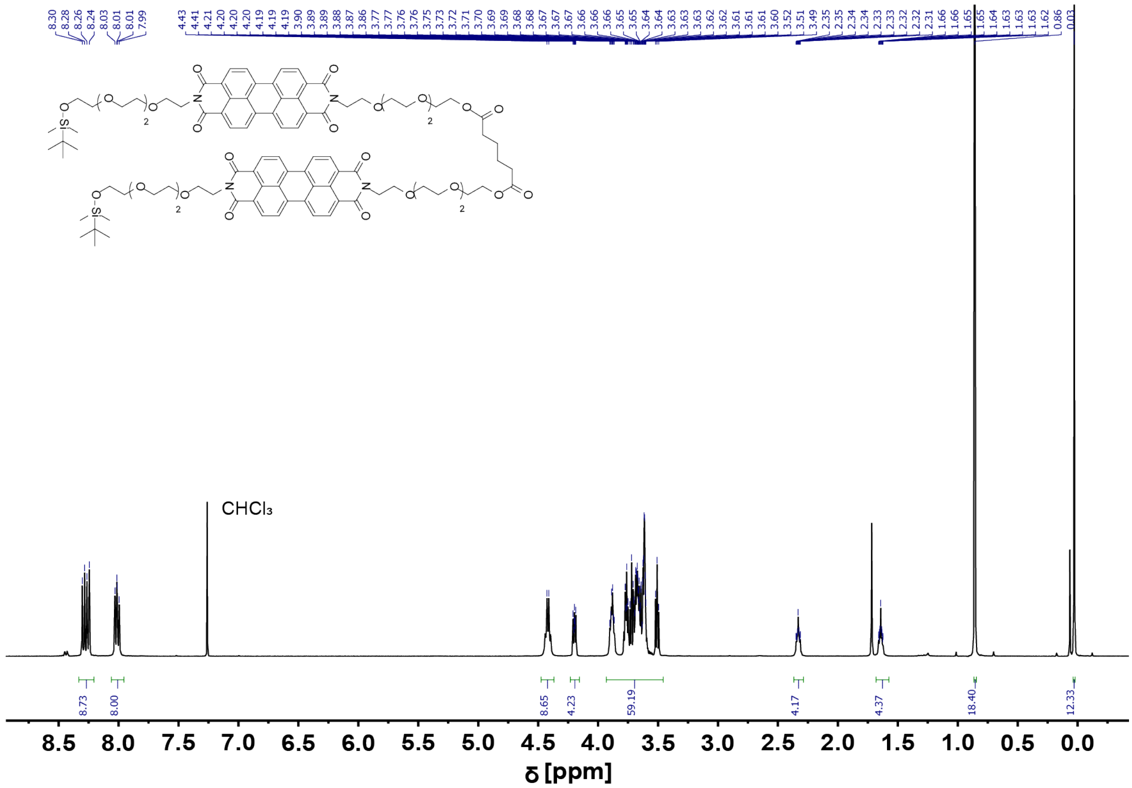
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **3**.



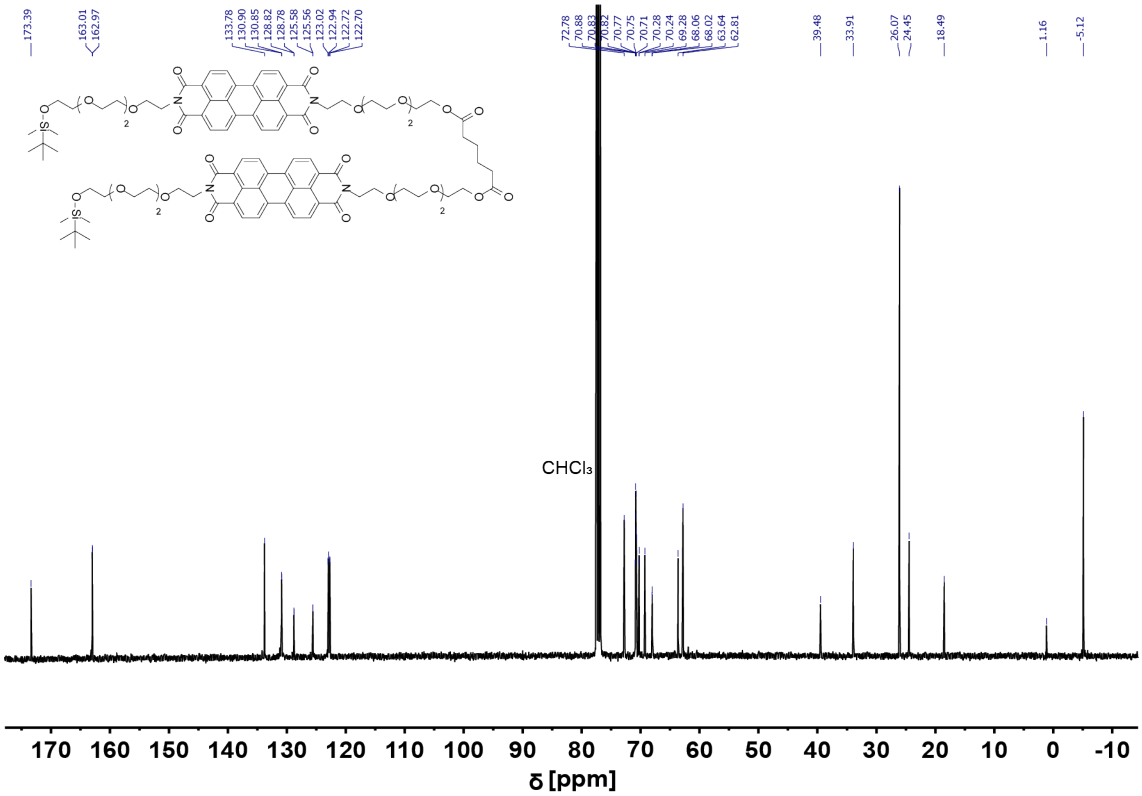
^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **3**.



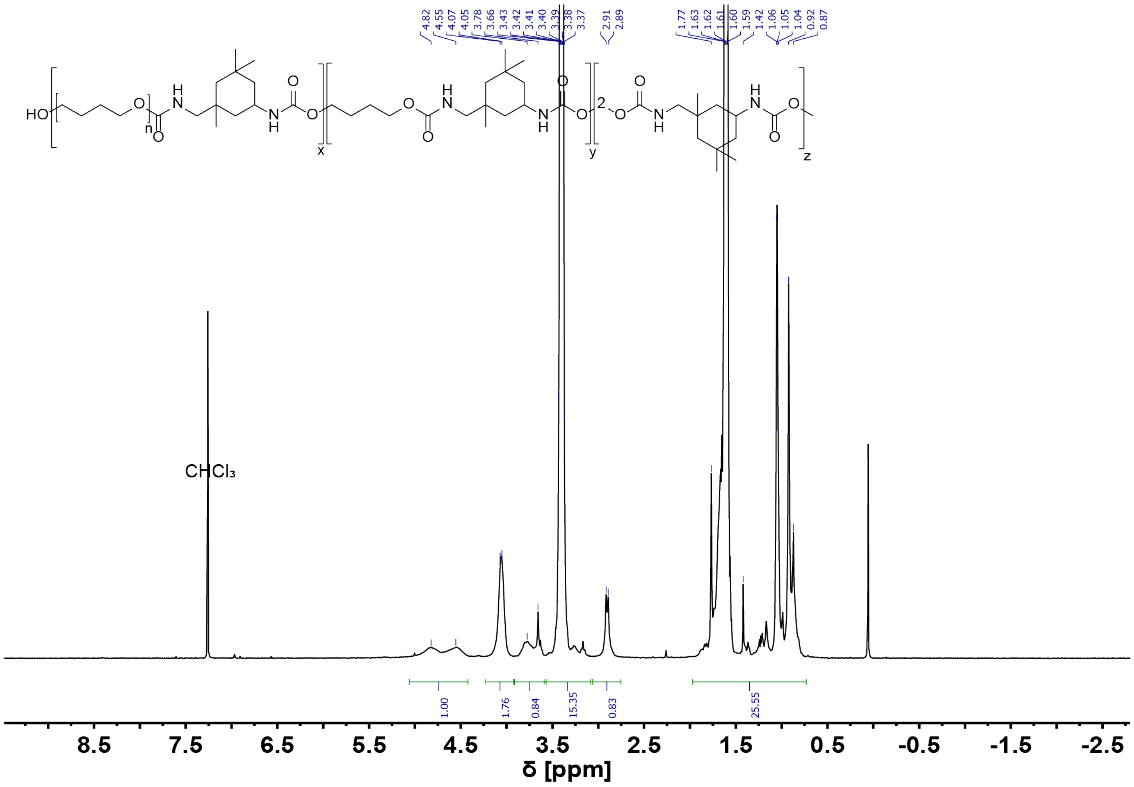
^1H NMR spectrum ($CDCl_3$, 400 MHz) of **4.**



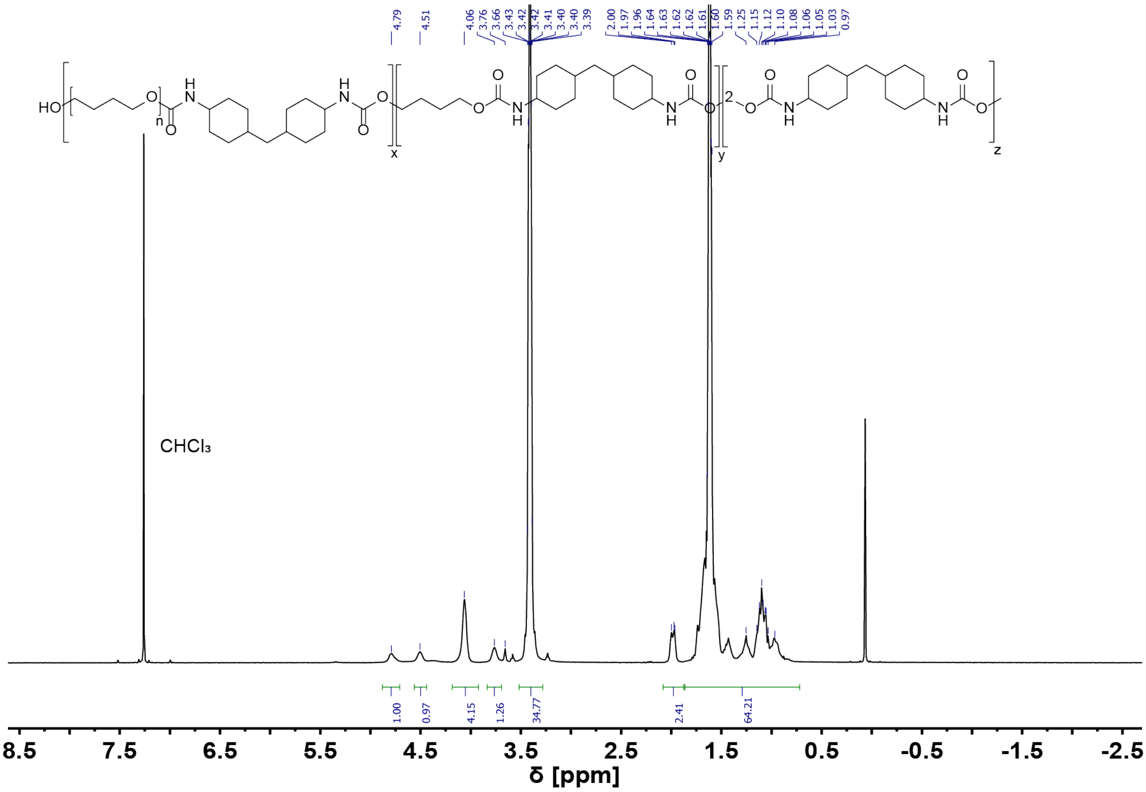
^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of **4**.



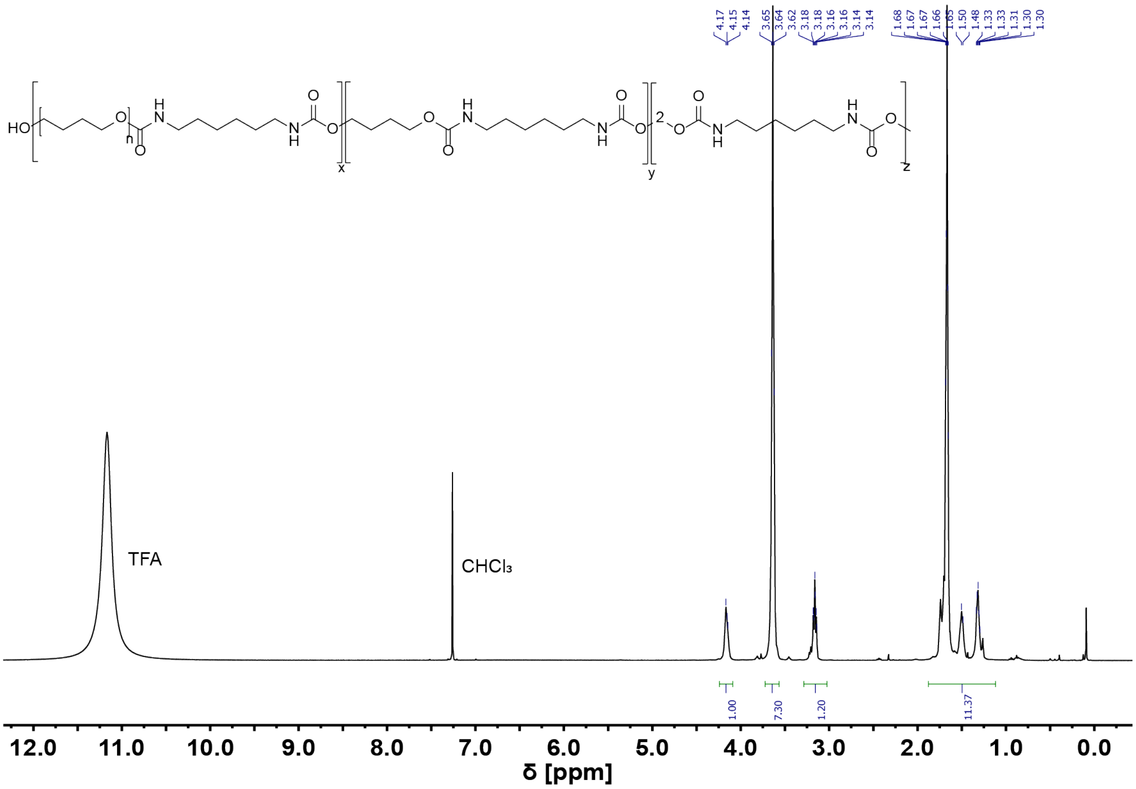
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **Loop-IDI-PU**.



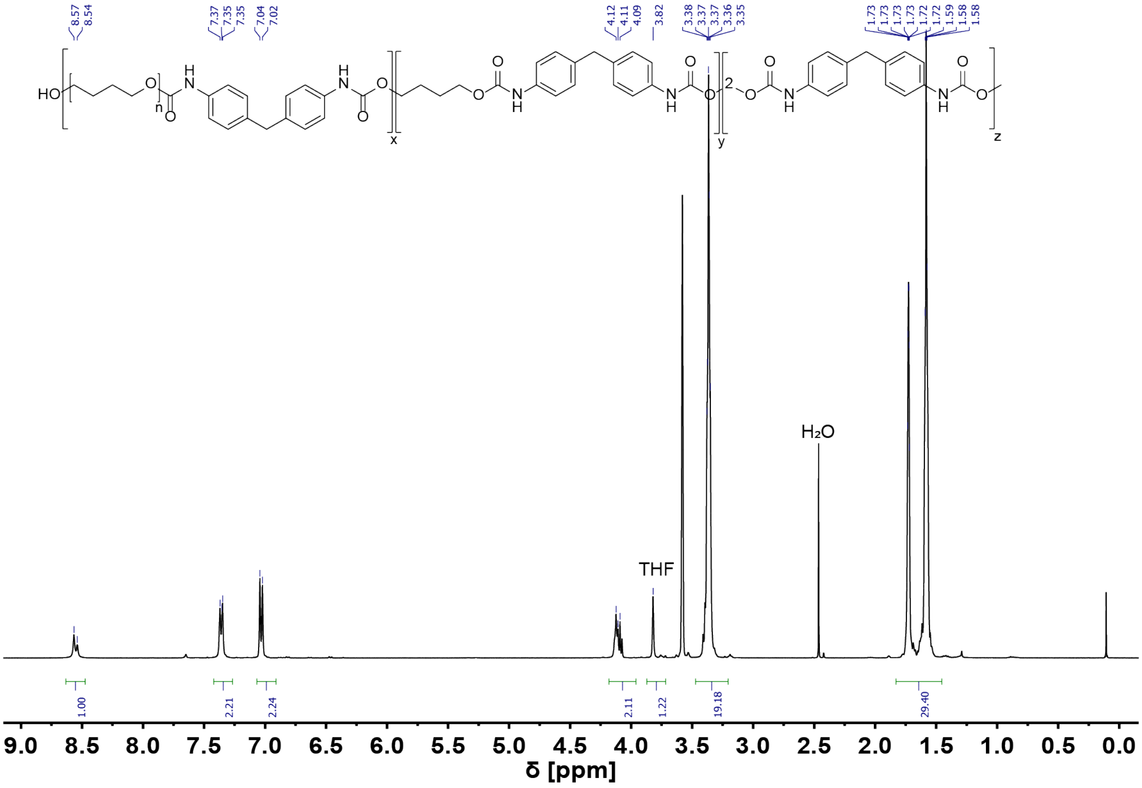
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **Loop-HMDI-PU**.



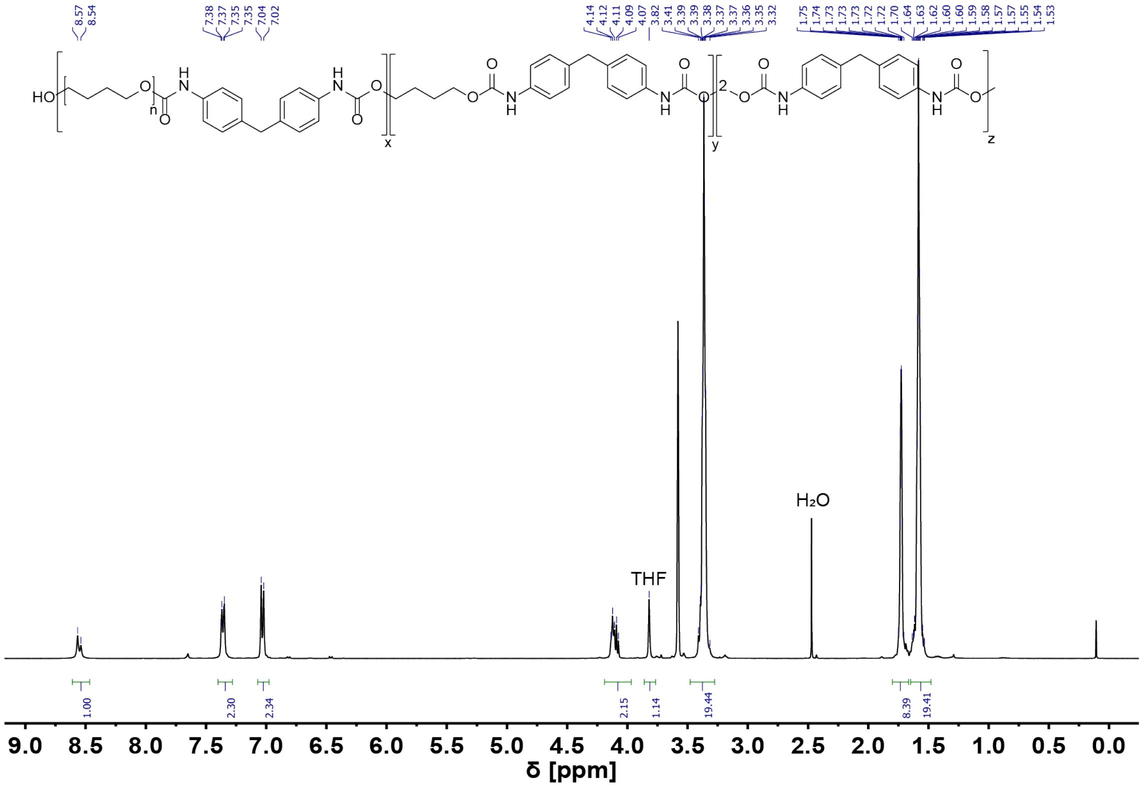
^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of **Loop-HDI-PU**.



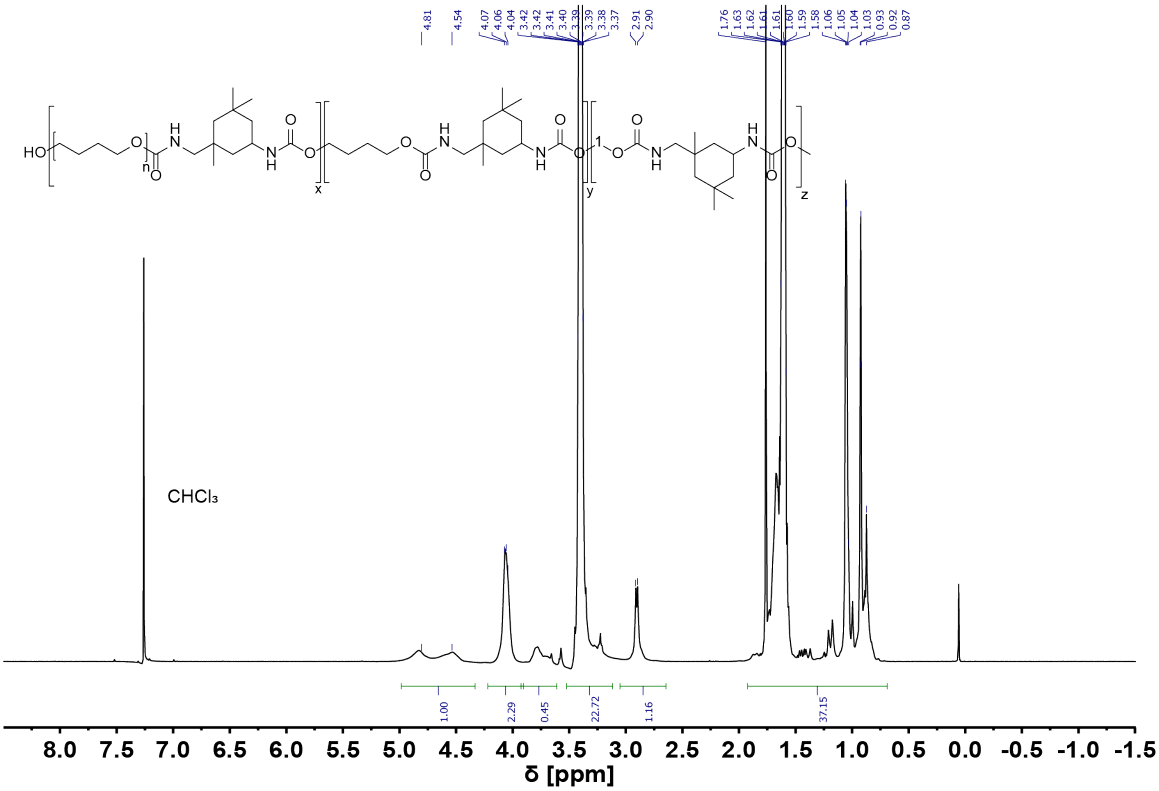
^{1}H NMR spectrum (THD-d$_8$, 400 MHz) of **Loop-MDI-PU 0.03 wt%**.



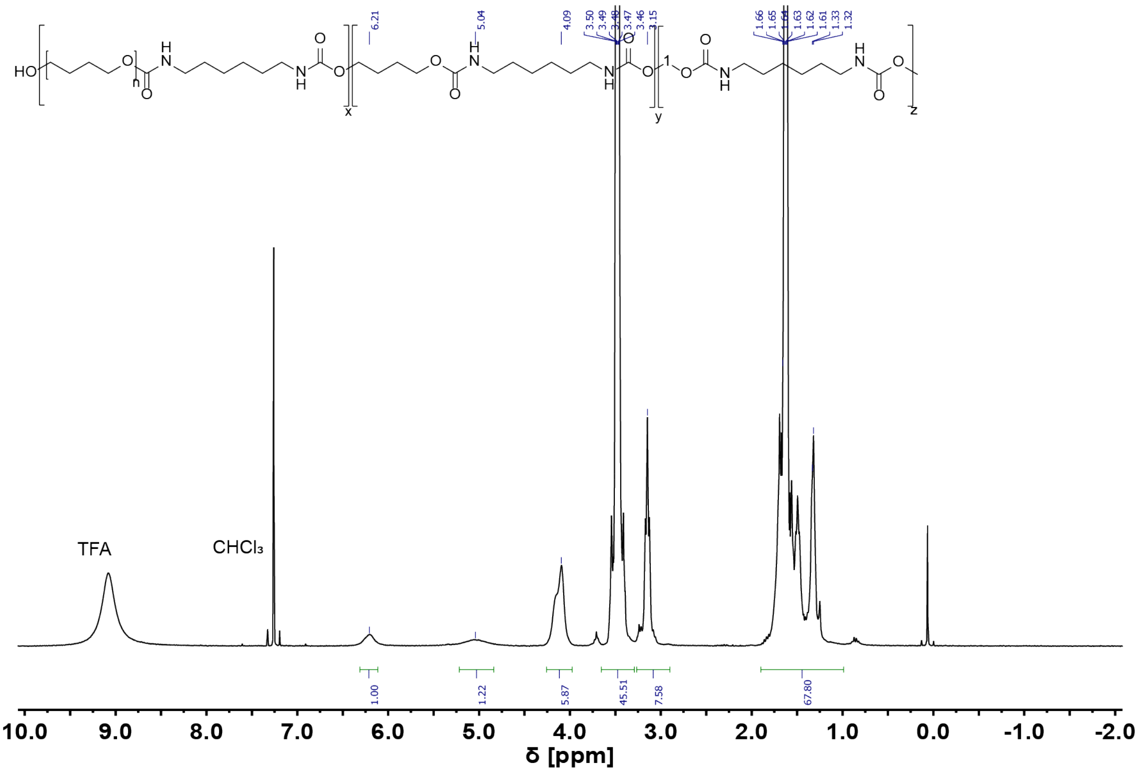
^{1}H NMR spectrum (THF-d_8, 400 MHz) of **Loop-MDI-PU 0.12 wt%**.



^{1}H NMR spectrum (CDCl$_3$, 400 MHz) of **PDI-IDI-PU**.



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **PDI-HDI-PU**.



6. References

1 J. J. Han, A. D. Shaller, W. Wang and A. D. Q. Li, *J. Am. Chem. Soc.*, 2008, **130**, 6974–6982.

2 H. Langhals, M. Rauscher and P. Mayer, *GSC*, 2019, **09**, 38–77.

3 H. Langhals and R. Ismael, *Eur. J. Org. Chem.*, 1998, 1915–1917.

4 B. Rybtchinski, L. E. Sinks and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2004, **126**, 12268–12269.

5 W. Wang, L.-S. Li, G. Helms, H.-H. Zhou and A. D. Q. Li, *J. Am. Chem. Soc.*, 2003, **125**, 1120–1121.

6 J. Chen, A. W. Ziegler, B. Zhao, W. Wan and A. D. Q. Li, *Chem. Commun.*, 2017, **53**, 4993–4996.