Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

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Detection of stress in polymers : mechanochemical activation of CuAAC click reactions in poly(urethane) networks

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Inhalt

1. Materials

All reactions were carried out under dry, inert argon atmosphere using common Schlenk techniques unless noted. All solvents were purchased in technical grade and were distilled before further use, while dry solvents were prepared using standard drying techniques and were subsequently degassed by freeze-pump-thaw-cycles. The chemicals were purchased from Sigma-Aldrich or VWR and used as received. Column chromatography was performed on Merck silica gel 60 (230 – 400 mesh). PTHF was purchased from Sigma Aldrich with a molecular weight of $M_n = 2900$ g * mol^{-1} and polydispersity of Đ = 1.60.

Fluorescence measurements were carried out in the bulk state on a Cary Eclipse fluorescence spectrometer of Agilent, fixing the samples with a solid sample holder between two quartz glass slides. Emission spectra were recorded after excitation at 377 nm with a maximum at 438 nm and repeated at least three times.

UV measurements were carried out via Perkin Elmer UV/vis Lambda 365 using Helma analytics quartz glass cuvettes (d = 10 mm) with a concentration of 0.20 mmol/L in THF.

NMR spectra were recorded on a Varian Gemini 400 or 500 spectrometer at 27°C. Chemical shifts (δ) are reported in ppm and referred to the solvent residual signal ($CDCl_3$ 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C; THF-d_8 3.58 and 1.72 ppm for ^{1}H as well as 67.2 and 25.3 ppm for ^{13}C; DMSO-d_6 2.50 ppm for ^{1}H and 39.5 ppm for ^{13}C).

GPC was performed on a Viscotek GPCmax VE 2001 with a set of a H_{HR}-H Guard-17369 and a GMH_{HR}-N-18055 main column in DMF with 0.75 mM $LiNTf_2$ at 60 °C. Detection was realized with a refractive index VE 3580 RI detector from Viscotek at 35 °C. The injection volume was 100 µL with a standard sample concentration of 5 mg mL^{-1} in DMF and the flow rate was adjusted to 1 mL min^{-1}. External calibration was done using poly(styrene) (PS) standards (purchased form PSS) with a molecular weight range from 1050 to 115 000 g mol^{-1}

ESI-TOF-MS measurements were performed on a Bruker Daltonics microTOF via direct injection with a flow rate of 180 µL h^{-1} using the negative mode with an acceleration voltage of 4.5 kV. Samples were prepared by dissolving sample in HPLC grade solvent at a concentration of 1 mg mL^{-1} without additional salt.

ATR-IR spectra were recorded on a Bruker Tensor Vertex 70 additionally equipped with a Golden Gate Heated Diamond ATR Top-plate. For analyzing data Opus 6.5 and OriginPro 8G SR4 (v8.0951) was applied.

Differential scanning calorimetry (DSC) experiments were performed in Al pans using a DSC 204 F1 Phoenix provided from NETZSCH. Samples were measured in a temperature range of -40 °C to 180 °C with a heating rate of 10 K min $^{-1}$ and analyzing data interpretation was accomplished using Proteus Thermal Analysis (V 5.2.1). The crystallinity was determined via equation (**equation S4** with 172 J/g as ΔH_m for 100% crystallinity[1].

Extensional oscillatory and rotational rheology experiments of thin films were conducted on Anton Paar (Physica) MCR 101/SN 80753612 via Universal Extensional Fixture (UXF) at 20 °C. Therefore, the films with rectangular shape (40 x 15 x 0.15 mm) (containing 0.85 $\mu mol_{(Cu)}/g_{(sample)}$ were fixed in the UXF sample holder and subjected to oscillating stretch experiments. To investigate the influence of the strain rate towards the mechanochemical activation of the Cu(I)-bis(NHC) catalysts, the strain rate was varied from 0.25 Hz, 0.5 Hz, 0.75 Hz to 1.0 Hz, while keeping the deformation constant at γ = 60%. The deformation dependency of the mechanochmemical activation was investigated varying the deformation from 40%, 60% to 80% and keeping the frequency constant at 0.5 Hz. Crosslinking dependence investigations were done with a strain rate of 0.5 Hz and deformation of 80%.

2. Synthetic procedures

3.1 Synthesis of 3-(11-hydroxyundecyl)-1-methylimidazolium bromide

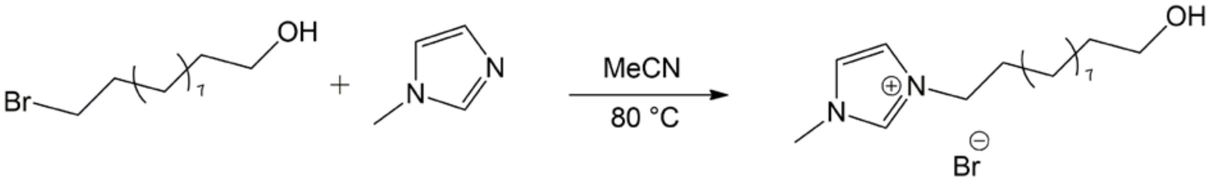


Figure S1. Synthesis of 3-(11-hydroxyundecyl)-1-methylimidazolium bromide.

1-Methylimidazole (3.01 mL, 38 mmol) was added to a suspension of 11-bromoundecan-1-ol (10.00 g, 40 mmol) in acetonitrile (MeCN) (50 mL) at room temperature (RT) and was stirred for 24 h at 80°C. The reaction mixture was allowed to come to RT and was diluted with diethyl ether (Et_2O) (120 mL). The resulting precipitate was filtered off, washed again with Et_2O (3 x 50 mL) and **1** was obtained as colorless solid after drying in high vacuum (12.41 g, 37.24 mmol, 98%).

^1H NMR (DMSO-d_6, 400 MHz,): δ 9.20 (*d*, *J* = 1.7 Hz, 1H), 7.80 (*t*, *J* = 1.8 Hz, 1H), 7.73 (*t*, *J* = 1.8 Hz, 1H), 4.31 (*t*, *J* = 5.1 Hz, 1H), 4.16 (*t*, *J* = 7.2 Hz, 2H), 3.86 (*s*, 3H), 3.36 (*td*, *J* = 6.5, 4.9 Hz, 2H), 1.83 – 1.69 (*m*, 2H), 1.39 (*t*, *J* = 6.7 Hz, 2H), 1.20 – 1.31 (*m*, 14H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 136.5, 123.5, 122.2, 60.6, 48.7, 35.7, 32.5, 29.3, 29.0, 28.9, 28.9, 28.8, 28.3, 25.5, 25.4. ESI-TOF MS (positive mode, MeOH, *m/z*) $[M]^+$ found 253.2279, simulated 253.2274 for $C_{15}H_{29}N_2O^+$.

3.2 Synthesis of Cu(I) mono(NHC) complex

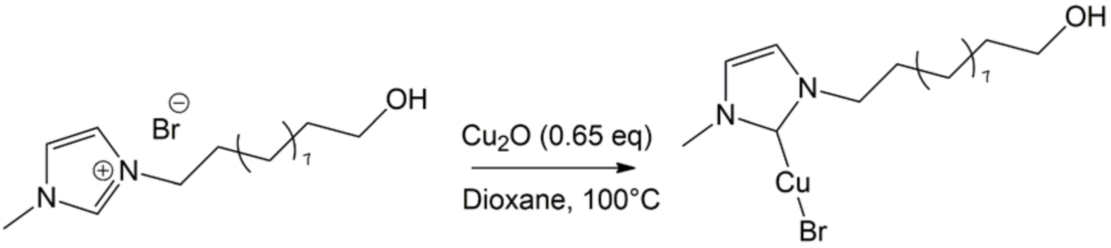


Figure S2. Synthesis of Cu(I) mono(NHC) complex.

3-(11-hydroxyundecyl)-1-methylimidazolium bromide (780 mg, 2.34 mmol) and copper(I)-oxide (220 mg, 1.52 mmol, 0.65 eq.) were suspended in dry 1,4-dioxane (4.8 mL) and was stirred at 100°C for 24 h. After cooling to RT, the reaction mixture was filtered twice, and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (DCM) (10 mL) and was precipitated in *n*-hexane (15 mL). Cu(I) mono(NHC) complex was obtained as a colorless solid (1.07 g, 2.70 mmol, 90%) after drying in high vacuum.

^{1}H NMR (THF-*d*$_8$, 500 MHz) δ 7.15 (d, *J* = 17.2 Hz, 2H), 4.13 (t, *J* = 7.0 Hz, 2H), 3.81 (s, 3H), 3.46 (q, *J* = 5.9 Hz, 2H), 3.26 (t, *J* = 4.7 Hz, 1H), 1.86 (p, *J* = 7.2 Hz, 2H), 1.45 (p, *J* = 6.9 Hz, 2H), 1.39 – 1.25 (m, 14H).^{13}C NMR (THF-*d*$_8$, 125 MHz) δ 171.3, 121.7, 120.5, 61.6, 50.7, 37.1, 33.1, 31.4, 29.6, 29.5, 29.5, 29.4, 29.1, 26.3, 25.9. ESI-TOF MS (negative mode, THF, *m/z*) $[M+Br]^-$ found 474.9815, simulated 474.9839 for $C_{15}H_{28}Br_2CuN_2O^-$.

3.3 Synthesis of Cu(I) bis(NHC) complex (**1**)

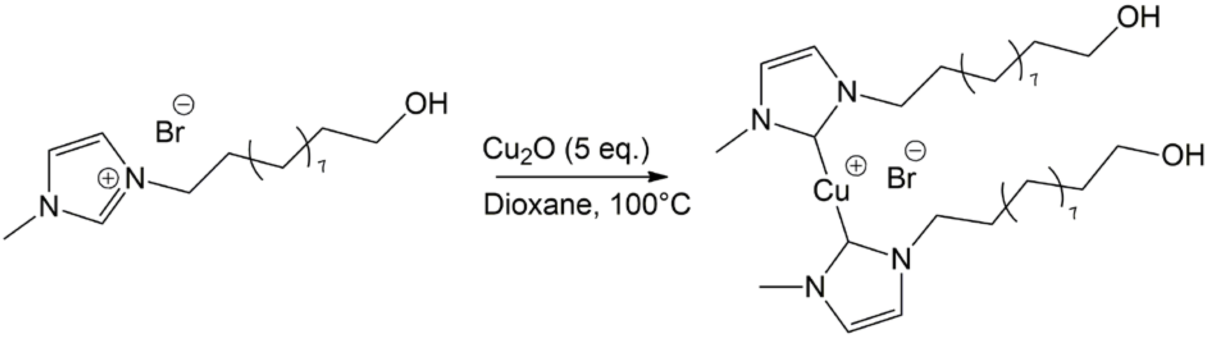


Figure S 3 Synthesis of Cu(I) bis(NHC) complex (**1**).

3-(11-hydroxyundecyl)-1-methylimidazolium bromide (2.0 g, 6.0 mmol) and copper(I)-oxide (4.3 g, 30.0 mmol, 5 eq.) were suspended in dioxane (50 mL) and was stirred at 100°C for 3 days. After cooling to RT the excess of Cu_2O was filtered off and the solvent was removed under reduced pressure. Compound **1** (1.55 g, 2.4 mmol, 40%) was obtained after column chromatography on silica by gradually changing the polarity of solvent from pure $CHCl_3$ to $CHCl_3$/MeOH 10/1 as a light yellow solid.

^{1}H-NMR (THF-d_8, 400 MHz) δ 6.27 – 6.23 (m, 4H), 3.51 (t, J = 7.2 Hz, 4H), 3.46 (q, J = 6.4 Hz, 4H), 3.35 (t, J = 5.2 Hz, 2H), 3.12 (s, 6H), 1.60 (p, J = 7.2 Hz, 4H), 1.47 (p, J = 6.9 Hz, 4H), 1.31 (d, J = 3.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.2, 111.1, 109.9, 62.9, 43.6, 32.8, 30.3, 29.5, 29.5, 29.4, 29.4, 29.3, 29.1, 26.5, 25.6. ESI-TOF MS (positive mode, THF, *m/z*) $[M]^+$ found 567.3616, simulated 567.3694 for $C_{30}H_{56}CuN_4O_2^+$

2.4 Synthesis of 8-azidonaphthalen-2-ol (**2**)

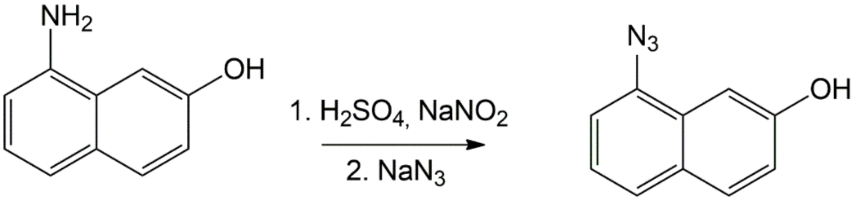


Figure S 4 Synthesis of 8-azidonaphthalen-2-ol (**2**).

HCl (8 mL, 36 wt%) was added dropwise to a suspension of 8-amino-2-naphthol (2.00 g, 12.5 mmol) in water (70 mL) and was cooled to – 5°C. A solution of $NaNO_2$ (1.30 g, 18.75 mmol) in water (10 mL) was added slowly and the mixture was stirred for 30 min at -5 °C. Over a time of 40 min a solution of NaN_3 (1.21 g, 18.75 mmol) in ice cold water (15 mL) was added and the reaction mixture was stirred at RT for 1 h. Afterwards the solution was extracted with Et_2O and washed with water. The combined organic layers were dried via Na_2SO_4 and the solvent was evaporated under reduced pressure. After purification via flash chromatography on silica (*n*-hexane/ethyl acetate 5:1) compound **2** (1.46 g, 7.88 mmol, 63 %) was obtained as a pale brown solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 (d, J = 8.8 Hz, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.39 (d, J = 2.5 Hz, 1H), 7.32 (t, J = 8.1 Hz, 1H), 7.22 (d, J = 7.1 Hz, 1H), 7.14 (dd, J = 8.8, 2.6 Hz, 1H), 5.10 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.7, 134.9, 129.8, 129.8, 127.5, 124.6, 123.3, 118.7, 114.5, 104.7. ESI-TOF MS (negative mode, THF:MeOH 99:1, *m/z*) $[M-H]^-$ found 184.0664, simulated 184.0516 for $C_{10}H_7N_3O^-$. FT-IR (ATR) 3316 (br), 2121 (s), 1631 (w), 1594 (m), 1524 (w), 1465 (m), 1394 (w), 1354 (w), 1294 (s), 1233 (m), 1199 (w), 1175 (s), 1137 (m), 1071 (w), 1012 (w), 916 (w), 884 (w), 858 (w), 827 (s), 780 (w), 759 (w), 738 (m), 721 (w), 666 (w), 634 (w).

2.5 Synthesis of 8-(4-(3-hydroxyphenyl)-1,2,3-triazol-1-yl)naphthalen-2-ol (**4**)

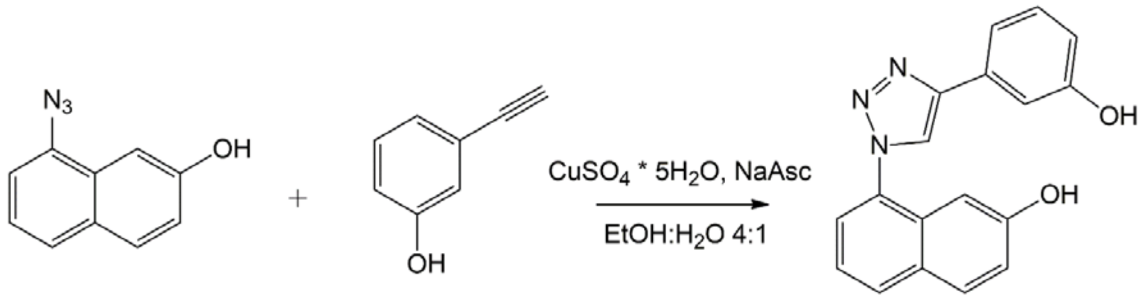


Figure S 5. Synthesis of (**4**).

A stock solution of $CuSO_4 * 5H_2O$ (54.0 µmol, 13.4 mg in 0.5 mL water) and a stock solution of sodium ascorbate (NaAsc) (80 0 µmol, 16.1 mg in 0.5 mL water) were added to a mixture of **2** (100.0 mg, 0.54 mmol) and 3-hydroxyphenylacetylene **3** (67.1 mg, 0.54 mmol) in EtOH (4 mL) and the resultant solution was stirred overnight at RT. The reaction mixture was diluted with water 15 mL, was extracted with $CHCl_3$ (3 x 10 mL), dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. After purification via column chromatography ($CHCl_3$:MeOH 20:1) compound **4** (154.0 mg, 0.51 mmol, 94%) was obtained as a yellow solid.

^{1}H NMR (DMSO-*d*$_6$, 400 MHz,) δ 10.01 (s, 1H), 9.59 (s, 1H), 8.99 (s, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.18 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.80 – 6.77 (m, 1H), 6.76 (d, *J* = 2.1 Hz, 1H).

^{13}C NMR (DMSO-*d*$_6$, 100 MHz) δ 158.3, 157.5, 147.0, 132.3, 132.1, 130.7, 130.5, 130.5, 130.4, 128.9, 124.7, 124.5, 122.3, 120.3, 116.7, 115.6, 112.6, 103.5. ESI-TOF MS (negative mode, THF:MeOH 99:1, *m/z*) $[M-H]^-$ found 302.0413, simulated 302.0935 for $C_{18}H_{13}N_3O_2^-$. FT-IR (ATR) 3136 (br), 1602 (m), 1516, 1453 (m), 1428 (w) , 1383 (w), 1356 (w), 1239 (s), 1200 (s), 1163 (w), 1080 (w), 1046 (w), 1000 (w), 968 (w), 910 (w), 871 (m), 829 (s), 782 (s), 743 (m), 717 (w), 687 (m), 663 (w), 573 (w).

3.6 Synthesis of 3-(1-(7-((hexylcarbamoyl)oxy)naphthalen-1-yl)-1H-1,2,3-triazol-4-yl)phenyl hexylcarbamate (**5**)

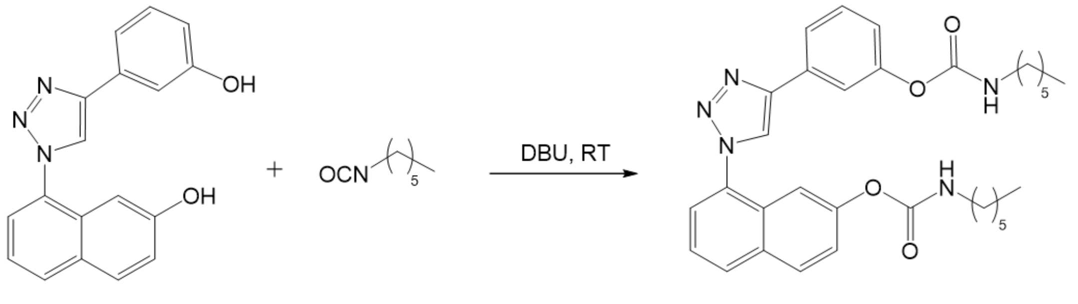


Figure S 6. Synthesis of (**5**).

Hexamethyleneisocyanate (187 µl ,1.28 mmol) was added to a mixture of **4** (150.0 mg, 0.49 mmol) followed by the addition of DBU (0.05 eq) and the resultant solution was stirred 4 h at RT. The reaction mixture was diluted with water 15 mL, was extracted with $CHCl_3$ (3 x 10 mL), dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. After purification via flash chromatography ($CHCl_3$:MeOH 20:1) compound **5** (234.0 mg, 0.42 mmol, 86 %) was obtained as a pale brownish solid.

^{1}H NMR (DMSO-*d*$_6$, 500 MHz) δ 9.17 (s, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 8.17 (d, *J* = 9.0 Hz, 1H), 7.83 (d, *J* = 7.4 Hz, 2H), 7.80 (t, *J* = 5.7 Hz, 2H), 7.75 – 7.66 (m, 2H), 7.54 – 7.46 (m, 2H), 7.25 (d, *J* = 2.0 Hz, 1H), 7.12 (dd, *J* = 7.9, 1.9 Hz, 1H), 3.08 (q, *J* = 6.8 Hz, 2H), 3.03 (q, *J* = 6.8 Hz, 2H), 1.52 – 1.39 (m, 4H), 1.36 – 1.18 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 6H), 0.83 (t, *J* = 6.7 Hz, 3H).^{13}C NMR (DMSO-*d*$_6$, 125 MHz) δ 154.7, 154.4, 152.2, 151.1, 146.5, 133.2, 131.9, 131.7, 130.7, 130.4, 130.3, 128.9, 125.3, 124.9, 124.9, 123.7, 122.3, 122.1, 119.2, 113.1, 40.9, 40.9, 31.4, 31.4, 29.7, 29.5, 26.4, 26.3, 22.5, 22.5, 14.4, 14.3.

3.7 Prepolymerization

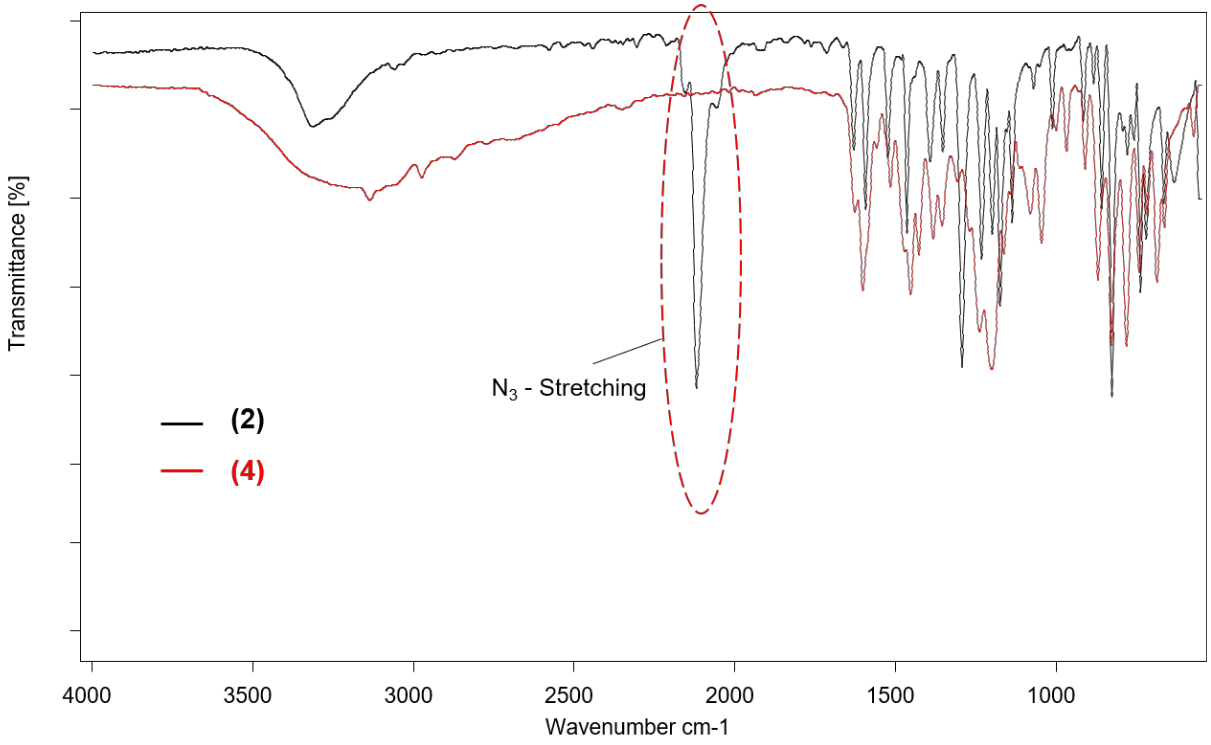


Figure S 7. FT-IR spectra of 8-azidonaphthalen-2-ol (**2**) and 8-(4-(3-hydroxyphenyl)-1,2,3-triazol-1-yl)naphthalen-2-ol (**4**).

3.7.1 Synthesis of prepolymers (**6**)

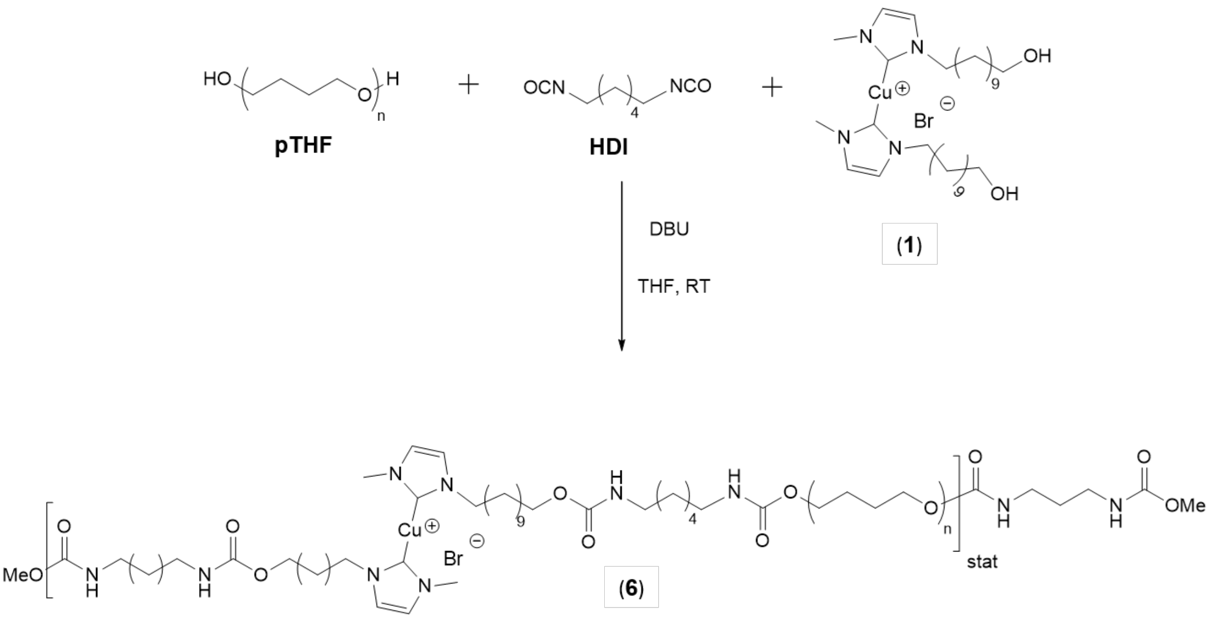


Figure S 8 Synthesis of **6** by prepolymerisation reaction of pTHF, HDI and **1**.

pTHF (3.00 g, 1.03 mmol) and **1** (2.70 mg, 4.00 µmol) were dissolved in THF (5 mL) followed by the addition of hexamethylenediisocyanate (HDI) (411.2 µL, 2.56 mmol) and catalytic amounts of 1,8-diazabicycloundec-7-ene (DBU). The reaction mixture was stirred at RT and after defined times, samples (~250 µL) were precipitated in MeOH (5 mL) and were investigated via GPC.

Table S1. Representative examples for molecular weight and polydispersity of PU during pre-condensation (**6**) process.

Time/min	**M_n[a)]/ g mol^{-1}**	**Đ**
0	2900	1.6
10	3800	1.6
20	4400	1.6
30	5100	1.7
40	5400	1.7
50	5900	1.7
60	6000	1.7

[a)] Determined via comparison of 1H-NMR and GPC measurements applying a correction factor of 0.68

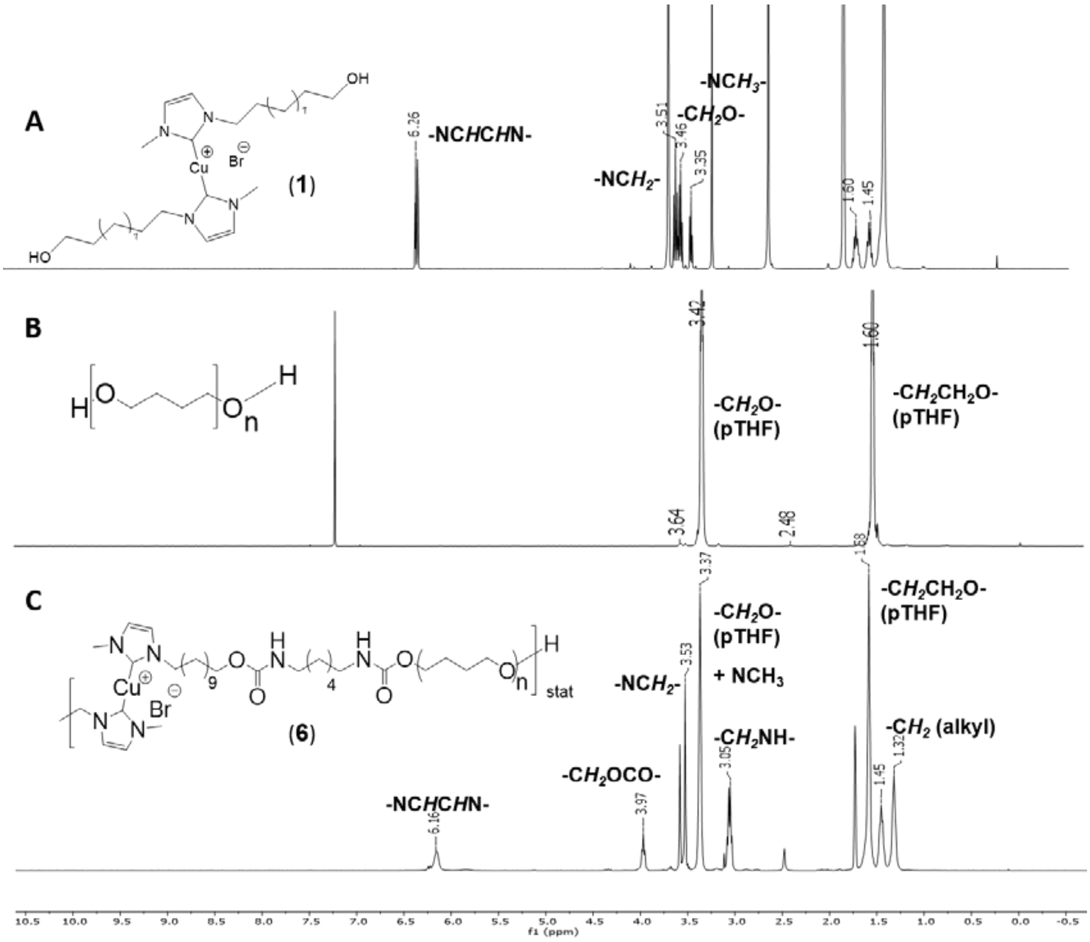


Figure S9. Comparison of ^{1}H-NMR spectra of **1** (A), pTHF (B) and precondensate **5** during prepolymerization reaction (in ratio 2:1 pTHF : (**3**)).

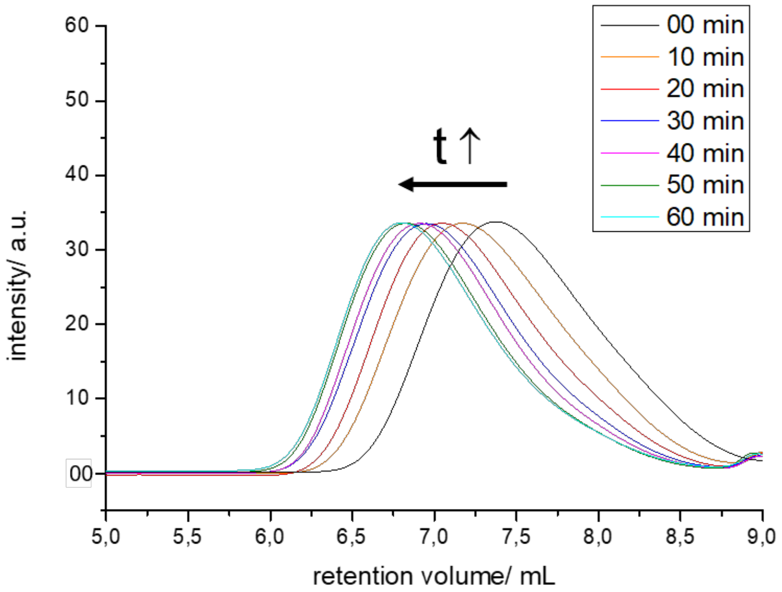


Figure S10. Representative GPC traces of prepolymers (**6**) with increasing reaction time.

3.7.2 Mechanochemical activation

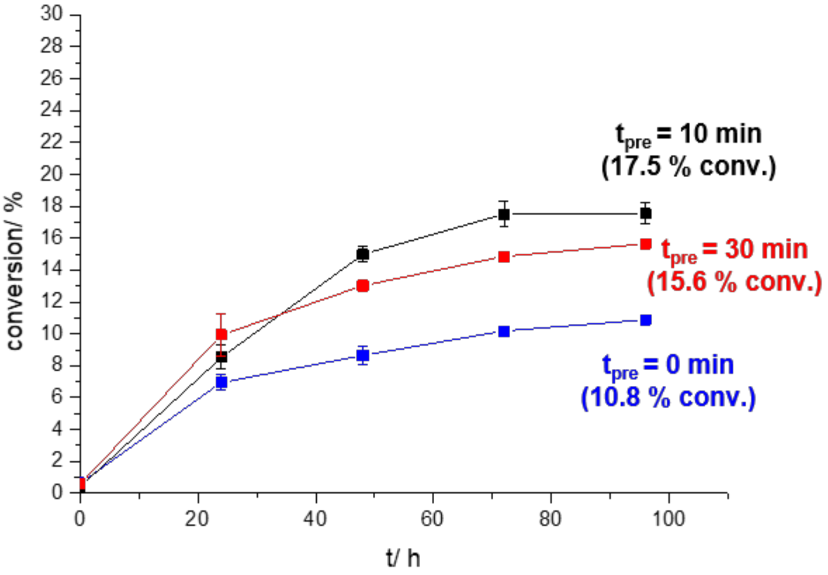


Figure S11. Prepolymerization time dependence of mechanochemical activation.

The mechanochemical activation of PU networks with different prepolymerization times were done in accordance to our standard protocol varying the time of adding TMP during synthesis. Figure S10 shows the activation curves of PU networks in which with no prepolymerization leads to the lowest conversion (blue curve) due to the faster oligomerization reaction of low molecular weight components (HDI,TMP,(**1**)). Accomplishing a prepolymerization reaction with a time of 10 min results to a chain extended copper(I)-bis(NHC) complexes which can finally crosslink by the trivalent TMP crosslinker, enhancing the mechanochemical activation (black curve). Longer pre-condensation time of 30 minutes results in a lower mechanochemical response (blue curve), presumably due to increased loops during the network formation, impair the force transmission in all direction and prevent an optimal force yield.

Synthesis of PU networks (**PUXX**)

In a representative procedure e.g. for **PU60**, the pre-condensate was formed dissolving pTHF (3.0 g, 1.03 mmol) and **1** (2.0 mg, 3.00 μmol) in THF (5 mL) followed by the addition of hexamethylenediisocyanate (HDI) (411.2 μL, 2.56 mmol) and catalytic amounts of DBU. The reaction mixture was stirred at RT and after a 10 min, trimethylolpropane (TMP) (83.3 mg, 0.62 mmol) dissolved in THF (1.00 mL) was added as crosslinker and the reaction mixture was stirred at RT until the desired viscosity was reached (absence of capillary attraction). After **2** (5.5 mg, 0.03 mmol) and 3-hydroxyphenylacetylene **3** (3.73 mg, 0.03 mmol) were added, the mixture was stirred again at RT for 5 min, the highly viscous liquid was poured in a Petri dish and was kept to condense further at RT for 1 h. The resulting foil (~0.1 mm thickness) were cut into shape (40 x 10 mm), were dried in high vacuum for 8 h in the dark and were stored under N_2 atmosphere for 1 day.

Table S2 Reaction conditions of polyurethane network synthesis

Comp.	**m** (pTHF) **g**	**n** (pTHF) **mmol**	**n (TMP)** (Cross) **mmol**	**m** (TMP) (Cross) **mg**	**n** (HDI) **mmol**	**V** (HDI) **µL**	**n (1) µmol**	**m (1) mg**	**n** (**2**/3) **µmol**	**m (2) mg**	**m (3) mg**
PU20	3.00	1.03	0.21	27.76	1.75	280	2.17	1.41	21.70	4.02	2.70
PU30			0.31	41.64	1.95	314	2.39	1.55	23.90	4.43	2.97
PU40			0.41	55.52	2.15	347	2.61	1.69	26.10	4.83	3.25
PU50			0.52	69.40	2.35	379	2.84	1.84	28.40	5.26	3.53
PU60			0.62	83.28	2.56	411	3.00	2.03	30.00	5.55	3.73
PU70			0.72	97.16	2.76	446	3.29	2.13	32.90	6.09	4.09
PU80			0.83	111.05	2.96	474	3.50	2.27	35.00	6.48	4.35

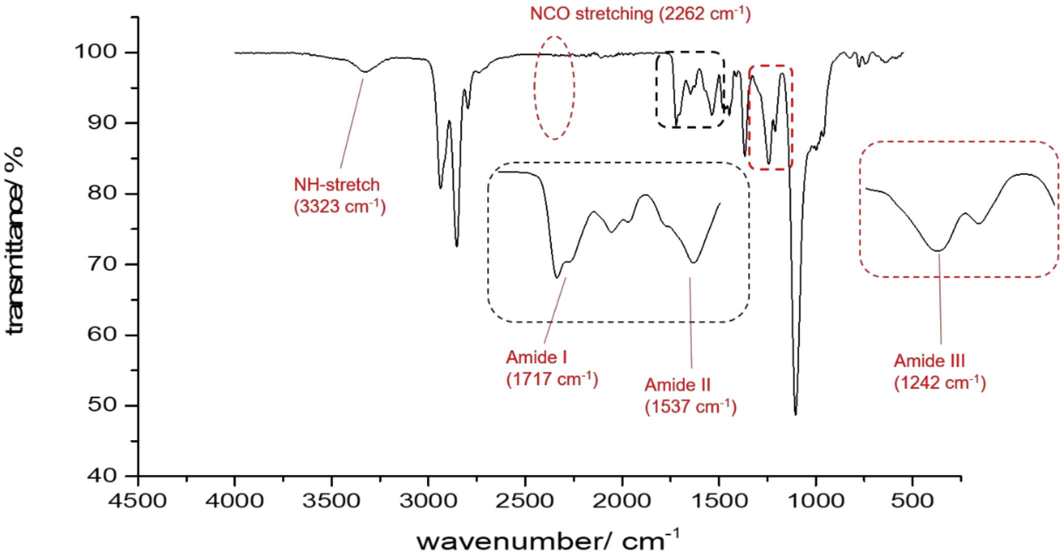
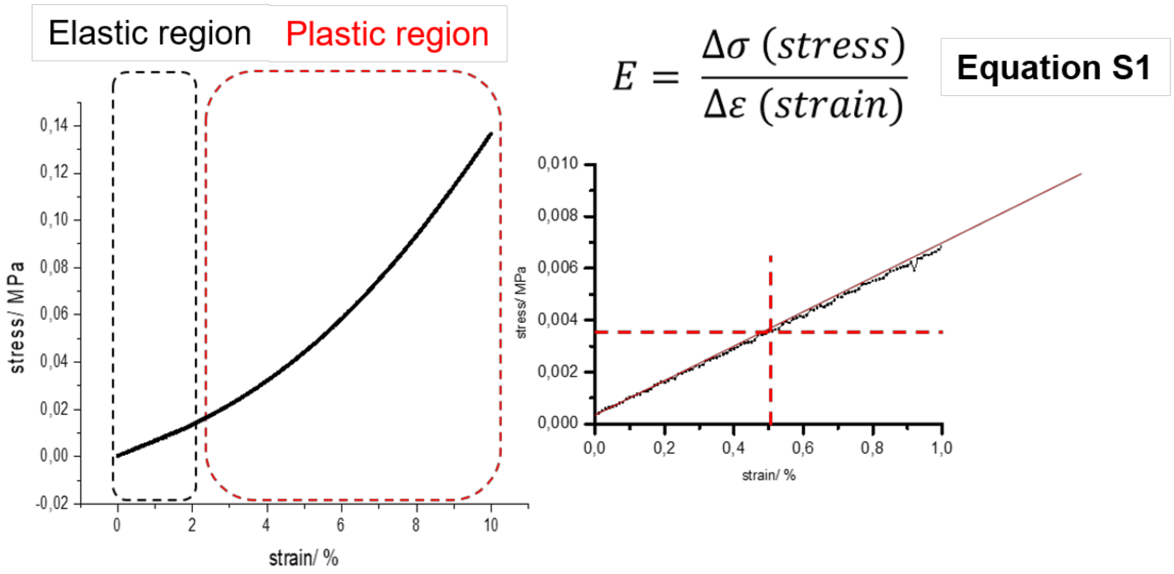


Figure S12. FT- IR spectrum (ATR) of **PU60**.

4. Mechanical properties of PU foils

4.1 Determination of E-modulus

The E-moduli determination of PU foils (**PU20 – PU80**) with different crosslinker densities was done via tensile rheological experiments. The applied strain (ranging from 0.01% to 2.00%) were correlated with the determined stress values and the E-modulus were calculated via linear regression in the low strain range from 0.01% to 0.5% according to **equation S1**.



$$E = \frac{\Delta\sigma\ (stress)}{\Delta\varepsilon\ (strain)}$$

Figure S13. Example for determination of E-modulus of **PU60**.

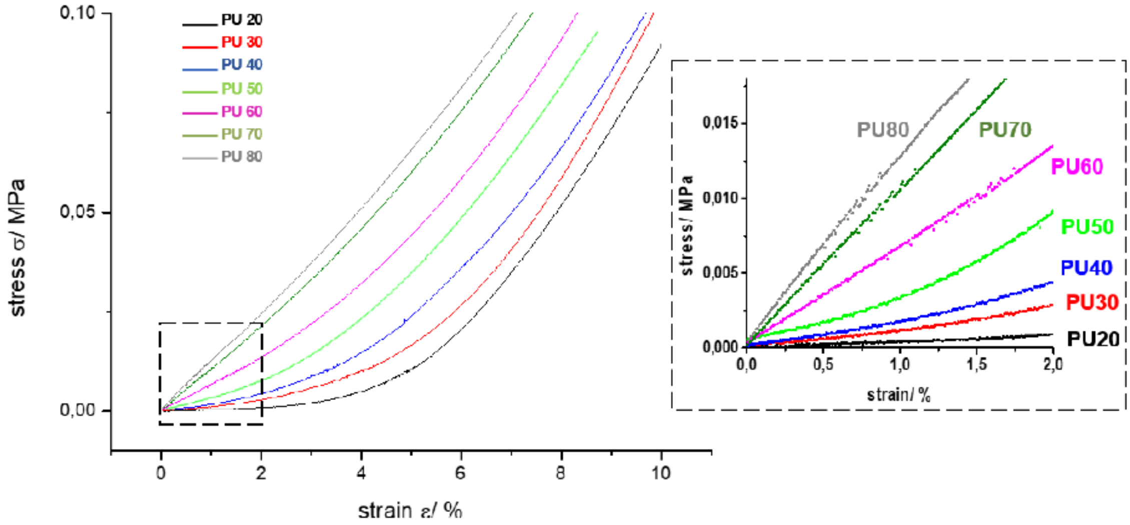


Figure S 14.) E moduli determination of PU networks with different OH-ratios

The crosslinking densities ν were calculated from tensile rheological experiments by means of G’ (**equation S2**) according to **equation S3** assuming a Poisson Ratio $\mu = 0.50$[2] .

$$G' = \frac{E}{2(1+\mu)} \qquad \textbf{(Equation S2)}$$

$$\nu = \frac{G'}{RT} \qquad \textbf{(Equation S3)}$$

Table S3. E-moduli of PU-networks and calculated G´ and ν.

Ent.	OH ratio a)	E module MPa	G´ module MPa	crosslinking density ν mol/m^3
PU20	0.2	0.04	0.01	4
PU30	0.3	0.10	0.03	12
PU40	0.4	0.19	0.06	24
PU50	0.5	0.32	0.11	45
PU60	0.6	0.68	0.22	90
PU70	0.7	1.00	0.34	139
PU80	0.8	1.20	0.41	168

a)OH ratio of bivalent (pTHF, (**2**)) and trivalent (TMP)

4.2 Determination of crystallinity (DSC analysis)

The crystallinity of the PU films (**PUXX**) were calculated according to **equation S4** assuming a melting enthalpy $\Delta H_{m0} = 172\ J * g^{-1}$ of pTHF for 100% crystallinity.[1]

$$\text{Crystallinity } \% = \frac{\Delta H_m}{\Delta H_{m0}} * 100\ \% \qquad \textbf{(Equation S4)}$$

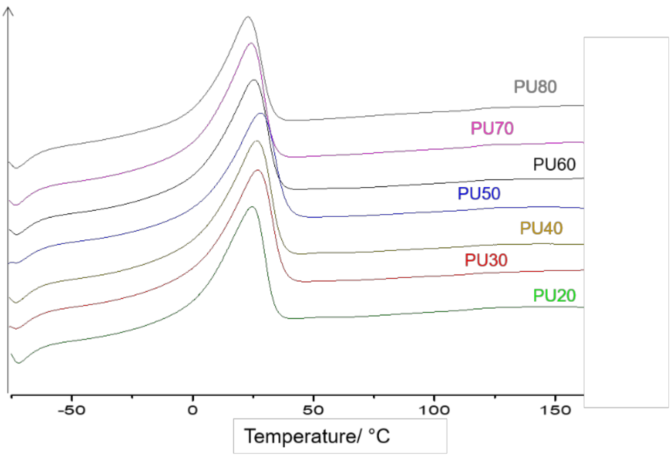


Figure S15. DSC curves (2nd heating cycle) of polyurethane networks (Heating rate 10 K/min).

Table S4. Melting enthalpy ΔH_m values and calculated crystallinity of PU networks

Ent.	OH ratio	ΔH_m J g^{-1}	Crystallinity %

PU20	**0.2**	46.2	26.8
PU30	**0.3**	45.3	26.2
PU40	**0.4**	44.4	25.8
PU50	**0.5**	43.5	25.2
PU60	**0.6**	41.1	23.8
PU70	**0.7**	40.2	23.3
PU80	**0.8**	38.3	22.3

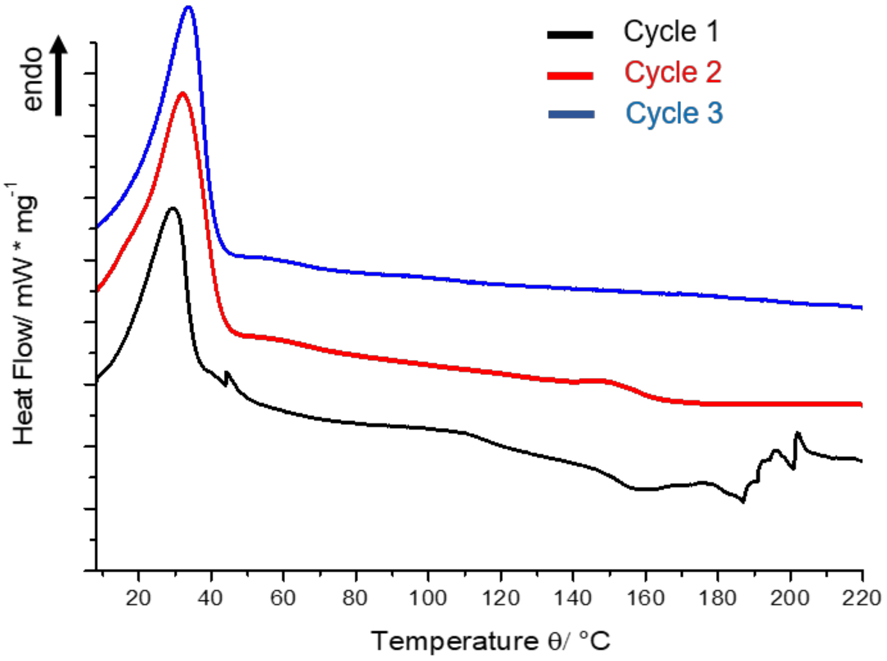


Figure S 16. Heating cycles (DSC) of PU 40 (Heating rate 2 K/min).

4.3 Swelling experiments

Swelling experiments were performed by placing the PU-foil (~50 mg) in THF (25 mL) and storing overnight at RT inside a closed system. Afterwards the excess of THF were removed and the foil was dried by means of a filter paper. After weighing the sample in swollen state, the solvent was removed by using high vacuum for at least 24 h until a constant weigh was reached. According to **equation S5** the THF uptake was calculated.

$$THF\ uptake\ \% = \frac{m\ (swollen\ sample)}{m\ (dried\ sample)} \qquad \textbf{(Equation S5)}$$

Ent.	**Comp.**	**OH ratio**	**THF uptake %**
1	**PU20**	0.2	1160
2	**PU40**	0.4	819
3	**PU60**	0.6	517
4	**PU80**	0.8	422

5. Optical properties

5.1 UV-vis and fluorescence measurements in solution

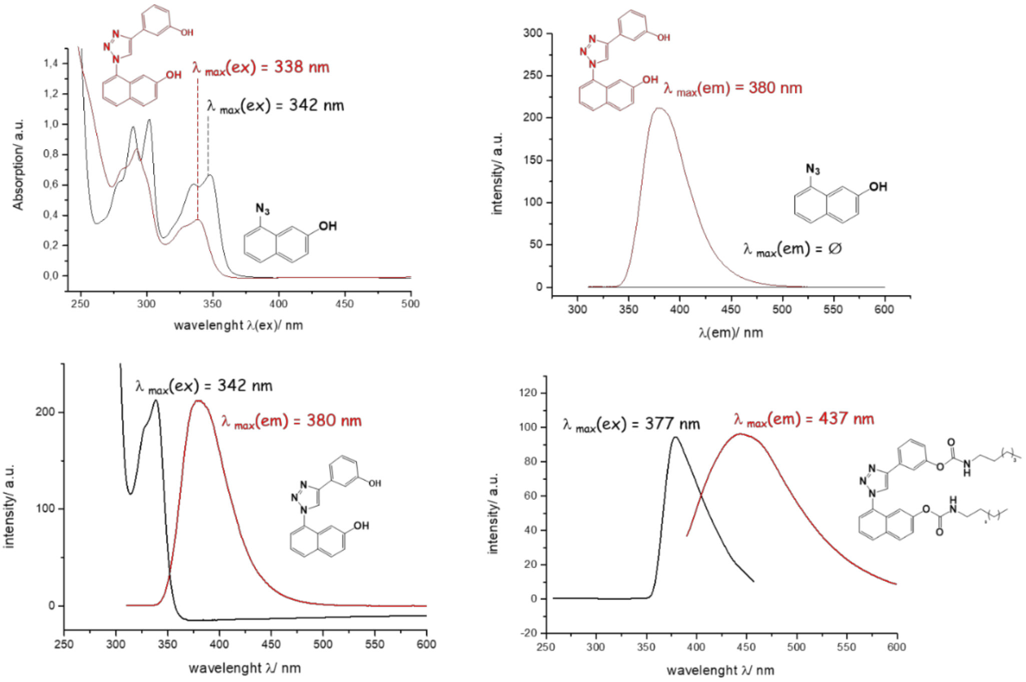


Figure S17. UV-spectra of used dyes in in THF.

5.2 Fluorescence measurements in solid state

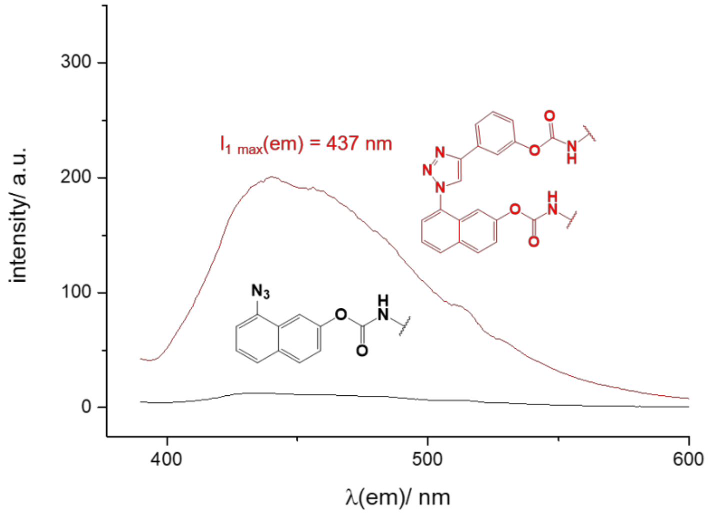


Figure S 18 Fluorescence spectrum (λ_{ex} = 377 nm) of compound **2** (black) and compound **4** (red) in solid state.

6. Mechanochemical activation of PU-networks

6.1 Calibration

The calibration of the fluorescence spectrometer was done embedding the clicked fluorogenic dye (**4**) in different concentration in the polyurethane matrix consisting out of pTHF, HDI, **1** and TMP in accordance to the synthetic procedure of **PU60** To compensate potential internal quenching effects of the dye, the overall concentration of naphthalene-based dyes (sum of mmol (**2)** and mmol (**4**)) were kept constant at 8.50 μmol/g$_{sample}$. **4** and the corresponding amounts of **2** (details see Table S5) were dissolved in dry THF (100 μL), were added to the **PUXX** reaction mixture mentioned above and were stirred for 5 min at RT before pouring into petri dish. After drying the PU foil with defined amount of dye were cut into the desired shape (40 x 20 x 0.15 mm) and dried in high vacuum. The foil was stored under N_2 atmosphere at RT for one day. Afterwards the fluorescence intensity was measured at 447 nm after excitation at 377 nm and plotted versus the conversion (calculated according to concentrations of dye **4** to dye **2**). Linear fitting yield equation **S6**, used for calculating the conversion of the mechanochemically triggered click reaction based on the fluorescence. For the calibration of PU with different crosslinking densities (**PU20-60**) fluorescence intensity was adapt to respective maximum amount of dye.

$$y = 8.0519\, x - 15.96 \qquad \textbf{Equation S6}$$

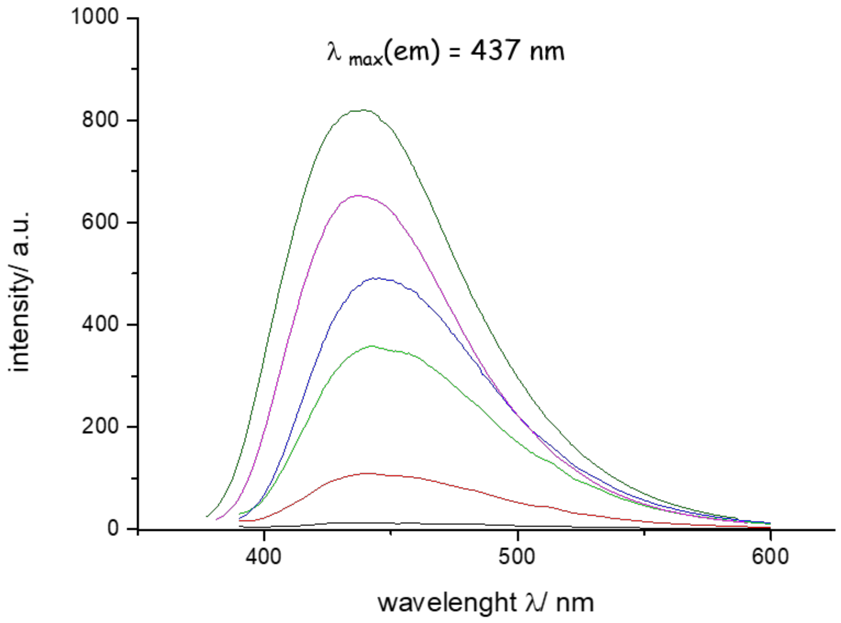


Figure S 19 Fluorescence spectrum of **PU 60** with different amounts of **4** (concentrations see Table S5).

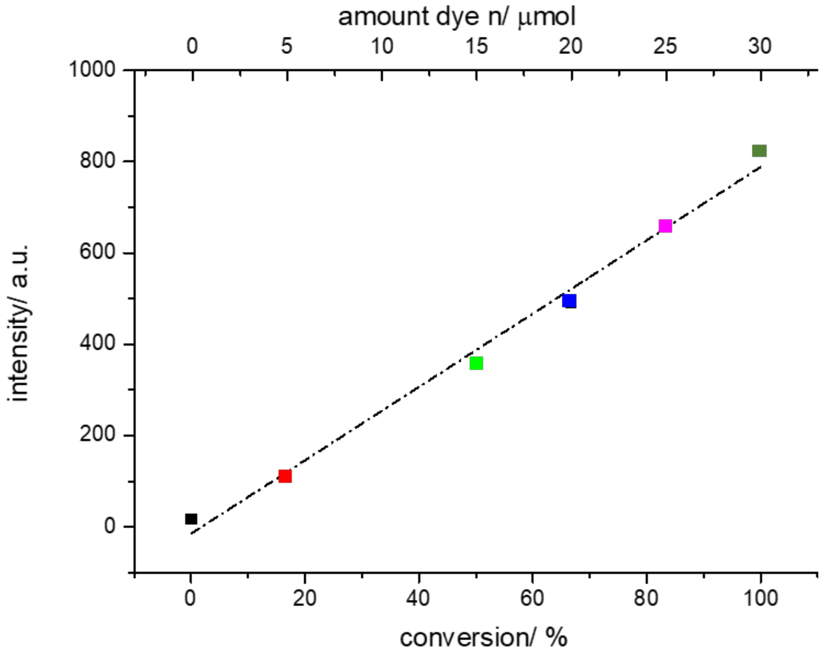


Figure S 20. Calibration plot of fluorescence intensity versus the concentration of the clicked dye (**4**) in the PU matrix and the calculated conversion during click reaction of **2** and **3**.

Table S 5. Detailed data for the calibration of the fluorescence intensity versus the concentration of (**3**) and (**5**) in PU matrix.

Ent.	**$n_{(4)}$ [mmol]**	**$m_{(4)}$ [mg]**	**$n_{(2)}$ [mmol]**	**$m_{(2)}$ [mg]**	**$I_{Fl.}$ (438 nm)** Sample1 **[a.u.]**	**$I_{Fl.}$ (438 nm)** Sample 2 **[a.u.]**	**$I_{Fl.}$ (438 nm)** Sample 3 **[a.u.]**	**$I_{Fl.}$ (438 nm)** Average **[a.u.]**	**conv. %**

1	0.000	0.00	0.03	5.55	15	15	15	15	0
2	0.005	1.52	0.025	4.63	108	110	112	110	17
3	0.015	4.55	0.015	2.77	352	355	364	357	50
4	0.020	6.06	0.010	1.85	492	492	492	492	67
5	0.025	7.58	0.005	0.92	652	657	662	657	83
6	0.030	9.09	0.000	0.00	821	822	826	823	100

6.2 Stress experiments via tensile rheology

Extensional oscillatory and rotational rheology experiments of thin films were conducted on Anton Paar (Physica) MCR 101/SN 80753612 via Universal Extensional Fixture (UXF) at 20 °C. Therefore, the films with rectangular shape (40 x 15 x 0.15 mm) (containing 0.85 $\mu mol_{(Cu)}$/ $g_{(sample)}$ were fixed in the UXF sample holder and subjected to oscillating stretch experiments. To investigate the influence of the strain rate towards the mechanochemical activation of the Cu(I)-bis(NHC) catalysts (**1**), the strain rate was varied from 0.25 Hz, 0.5 Hz, 0.75 Hz to 1.0 Hz, while keeping the deformation constant at γ = 60%. The deformation dependency of the mechanochemical activation was investigated varying the deformation from 40%, 60% to 80% and keeping the frequency constant at 0.5 Hz. Crosslinking dependence investigations were done with a strain rate of 0.5 Hz and deformation of 80%.

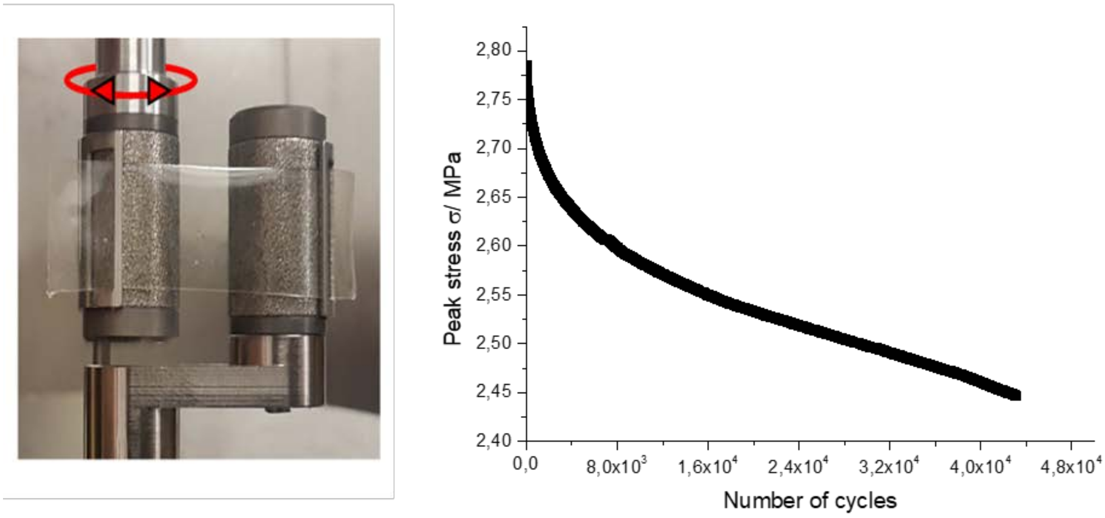


Figure S 21. Example for the loss of material strength during stress experiment (**PU60**).

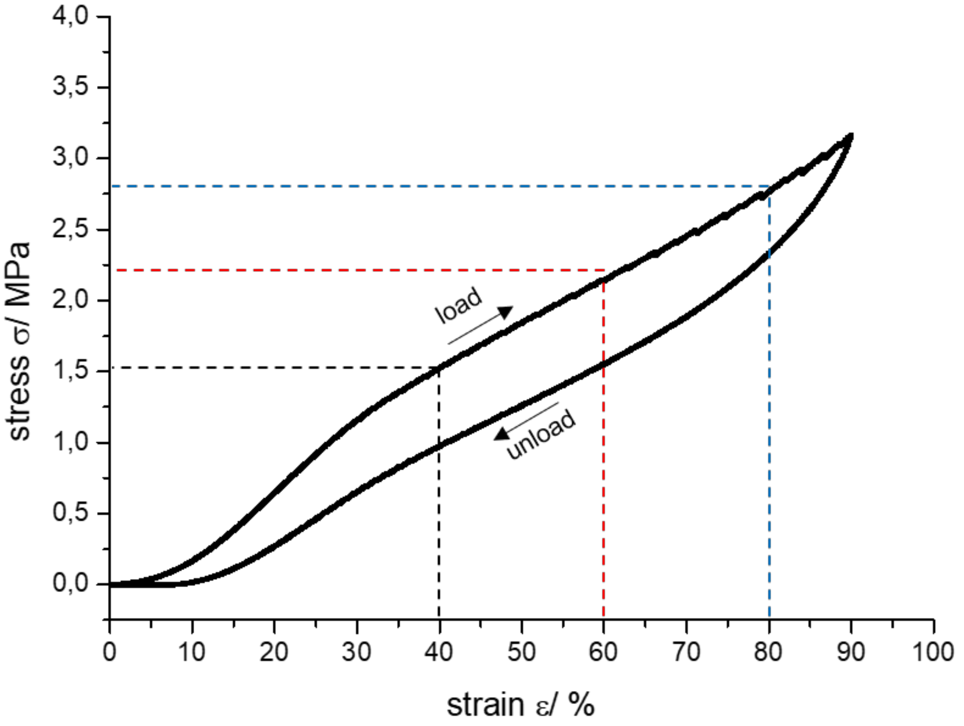


Figure S 22 Stress strain curve of **PU 60** and determination of nominal stress at different deformation.

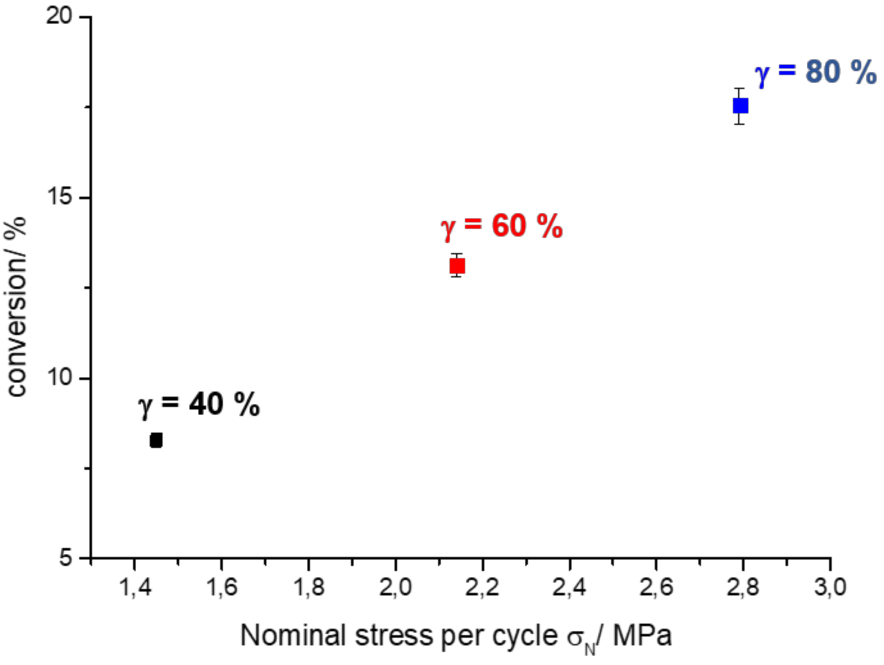


Figure S 23. Conversion versus nominal stress in **PU60** (F = 0.5 Hz).

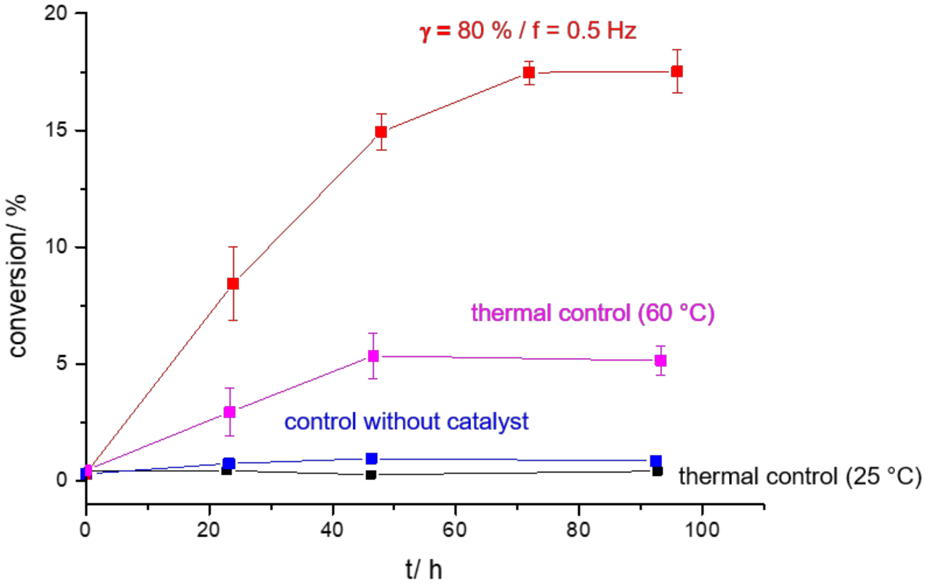


Figure S 24 Thermal control experiments (25°C and 60°C) as well as control experiment without catalyst during mechanical testing of **PU 60**.

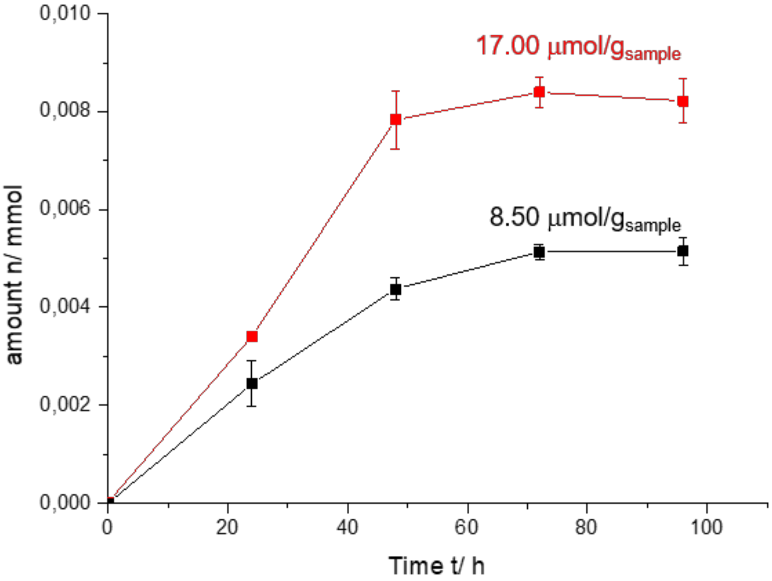


Figure S 25 Stress-induced ctivation of **PU 60** containing two different amoubts of catalyst with constant amounts of fluorogenic precursors (**3**,**4**) resulting the fluorescent dye (**5**) after stressing**.**

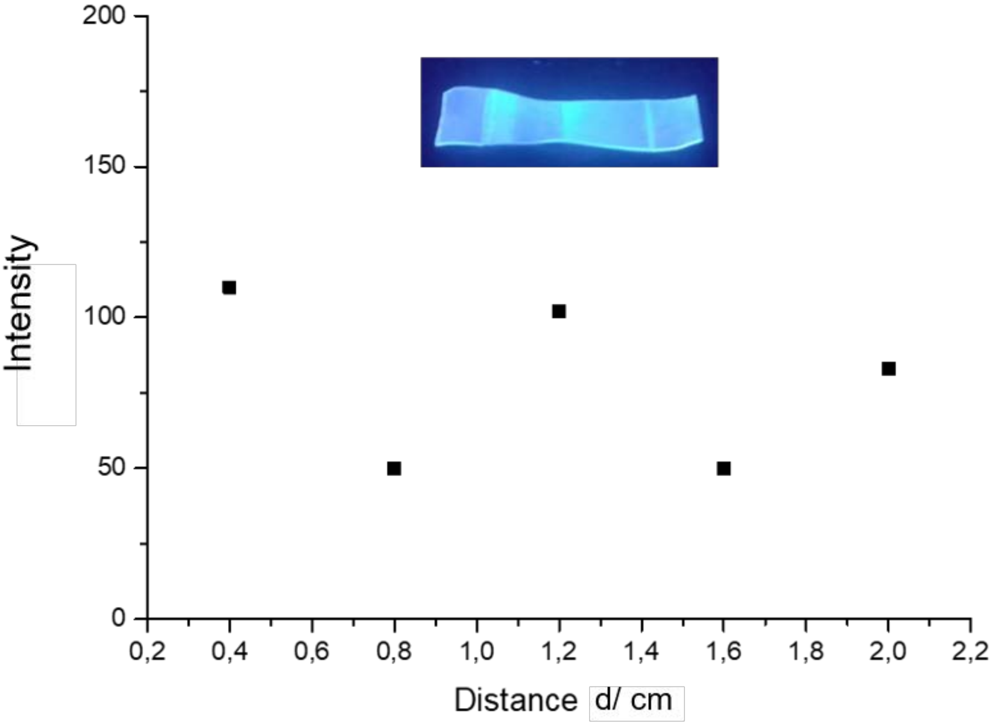


Figure S 26 Distribution of fluorescence intensity after stress experiment of PU **60**

7. NMR spectra

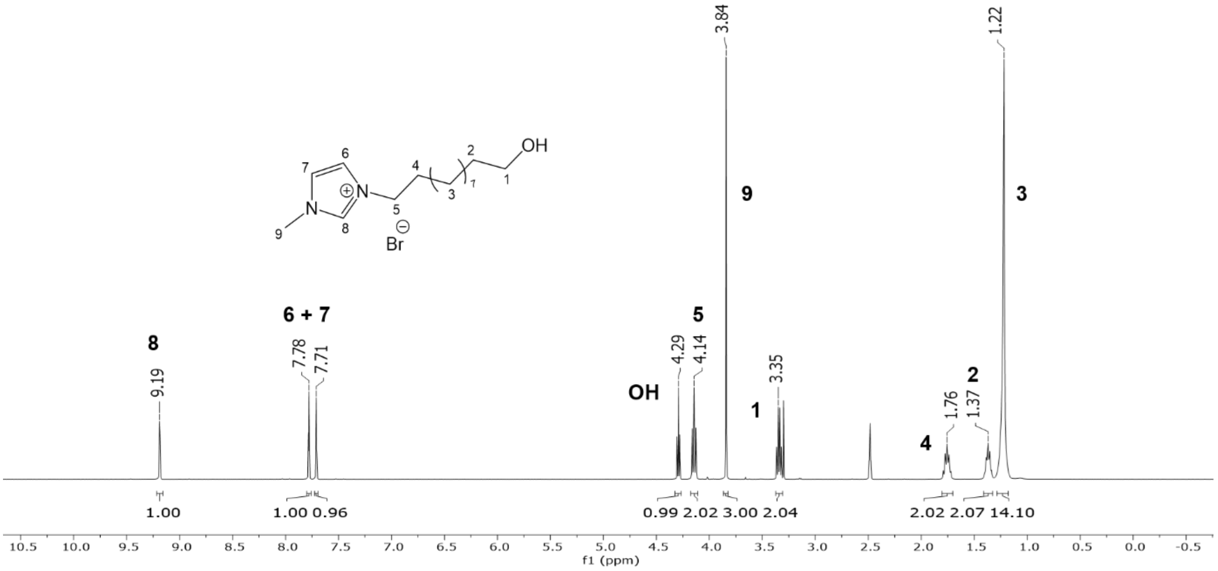


Figure S 27. ^{1}H-NMR spectra of 3-(11-hydroxyundecyl)-1-methylimidazolium bromide in DMSO-d$_6$.

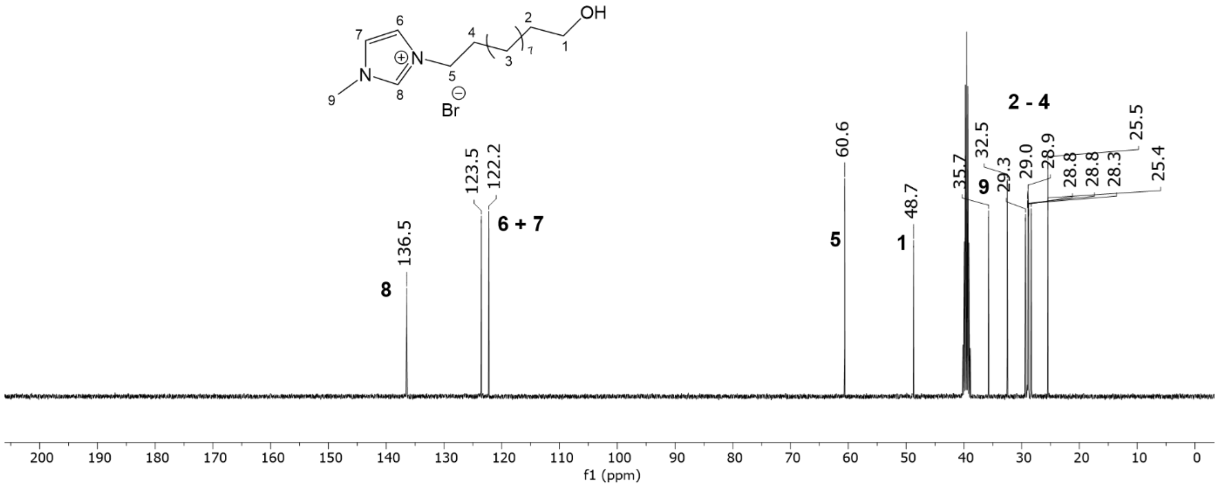


Figure S 28. ^{13}C-NMR spectra of 3-(11-hydroxyundecyl)-1-methylimidazolium bromide in DMSO-d$_6$.

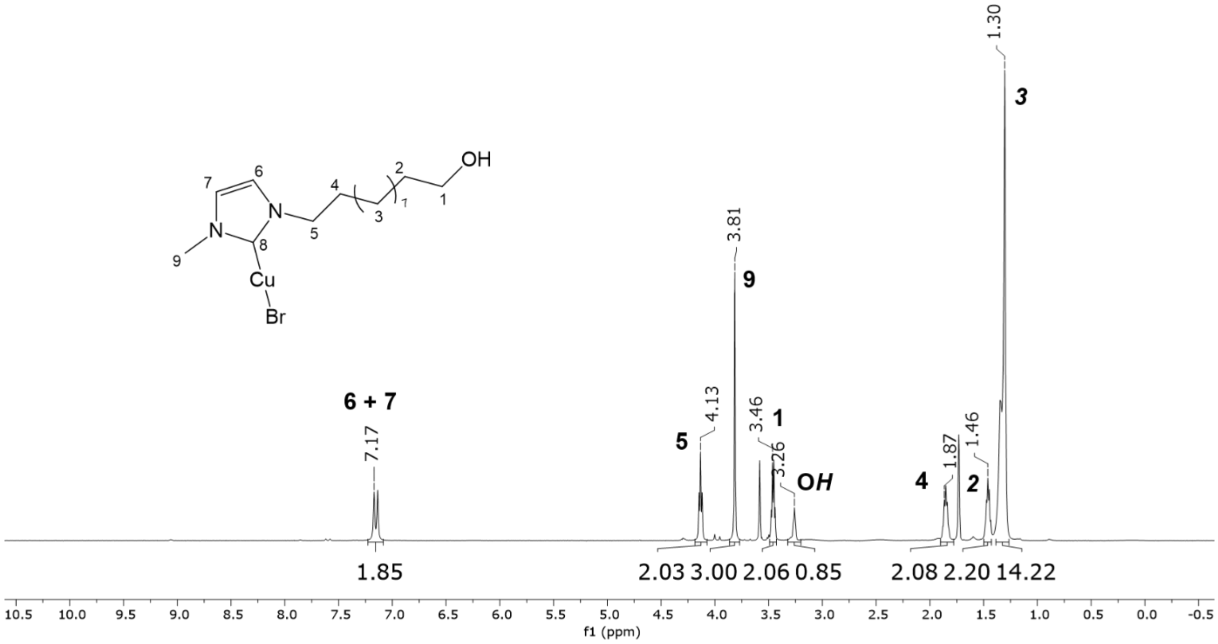


Figure S 29. ^{1}H-NMR spectra of Cu(I) mono(NHC) complex inTHF-d$_8$.

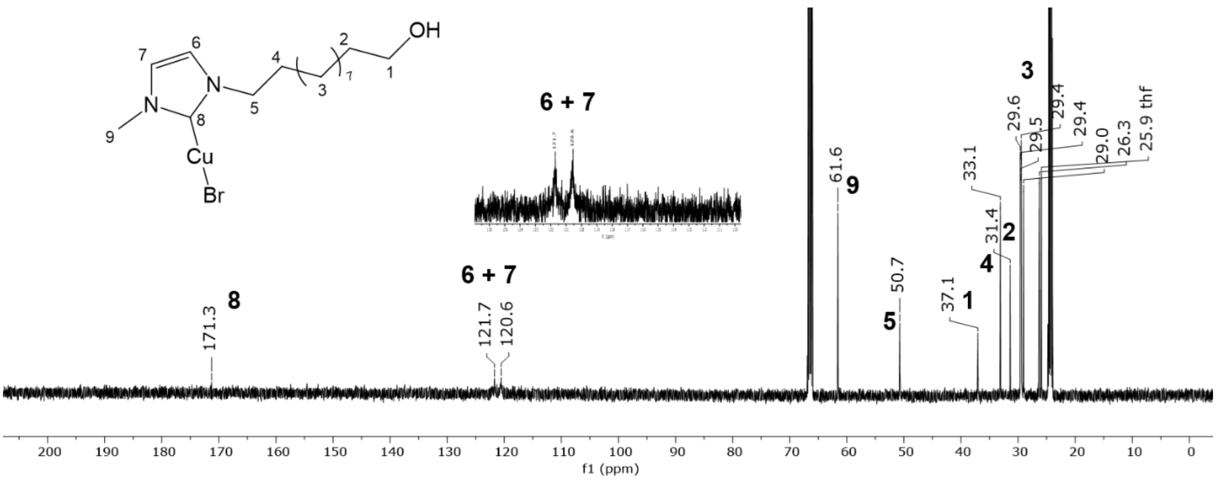


Figure S 30. ^{13}C-NMR spectra of Cu(I) mono(NHC) complex inTHF-d$_8$.

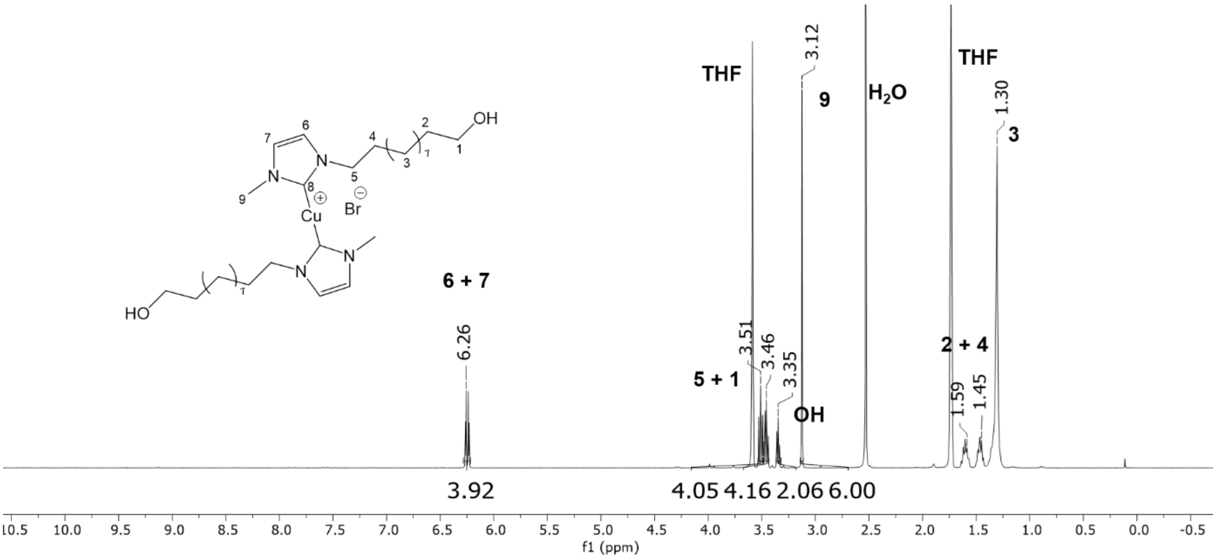


Figure S 31. ^{1}H-NMR spectra of compound (**1**) inTHF-d$_8$.

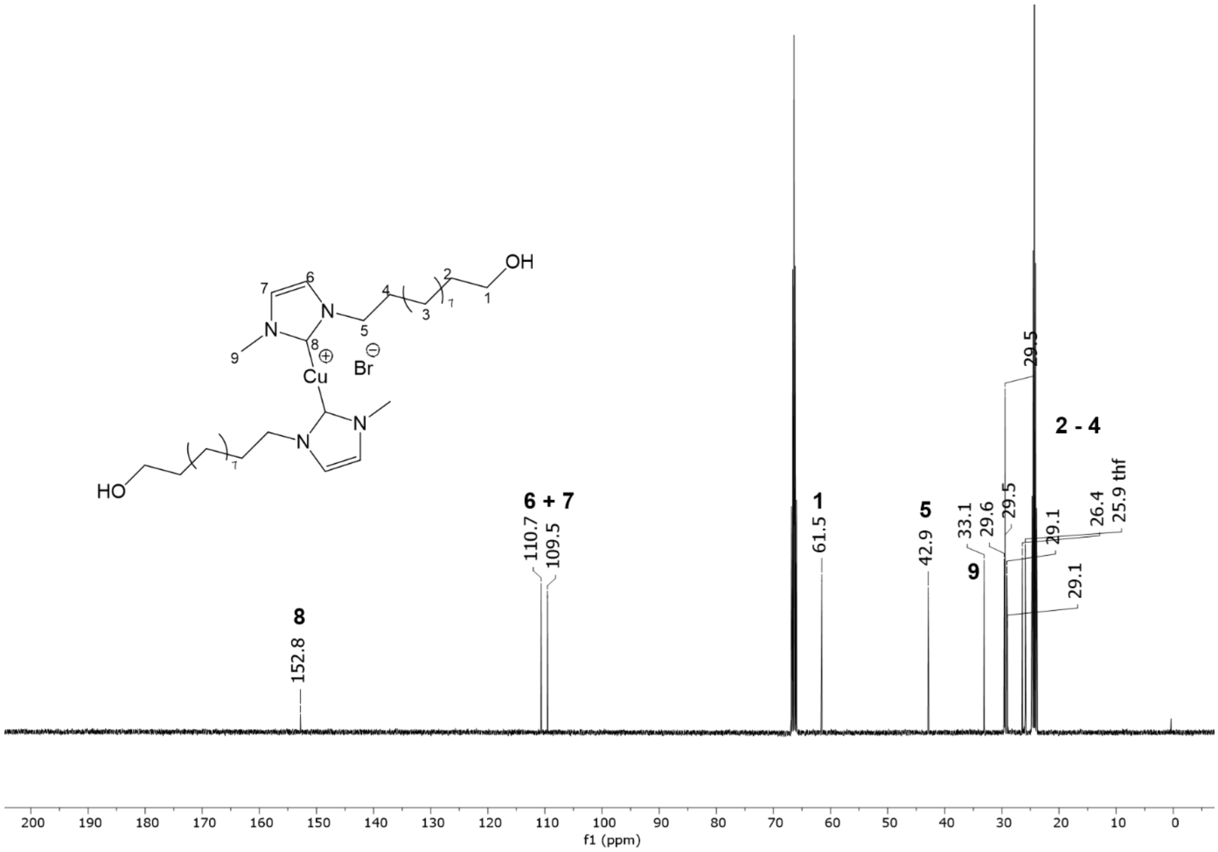


Figure S 32. ^{13}C-NMR spectra of compound (**1**) inTHF-d$_8$.

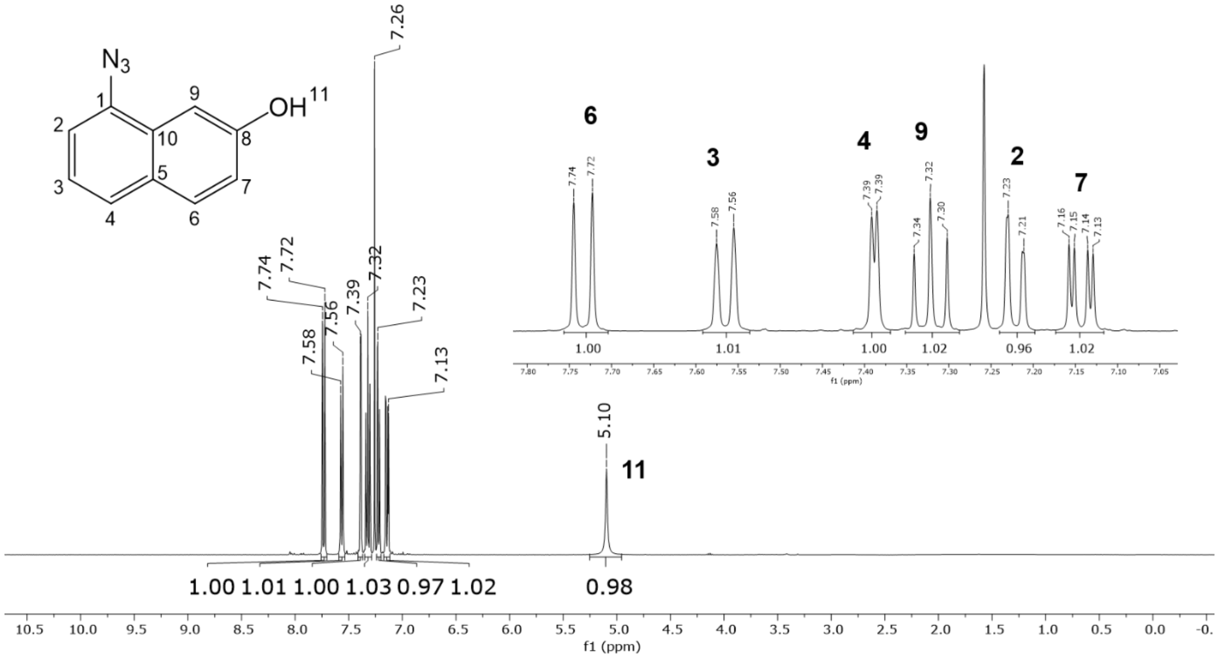


Figure S 33. ^{1}H-NMR spectra of compound (**2**) in CDCl$_3$.

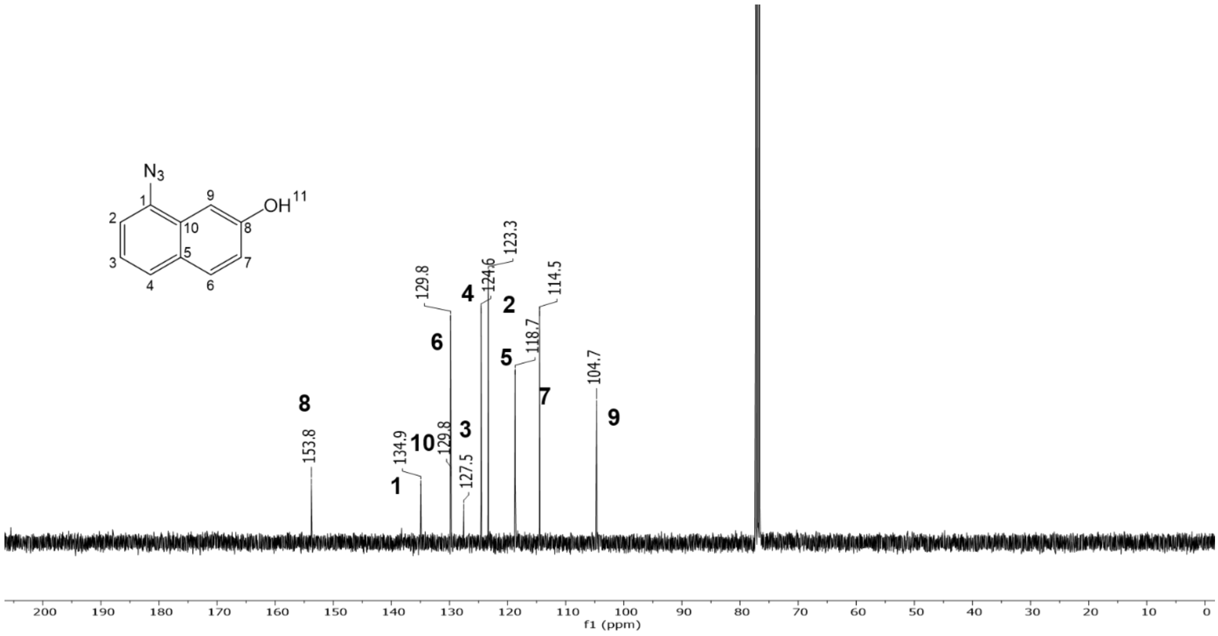


Figure S 34. ^{13}C-NMR spectra of compound (**2**) in CDCl$_3$.

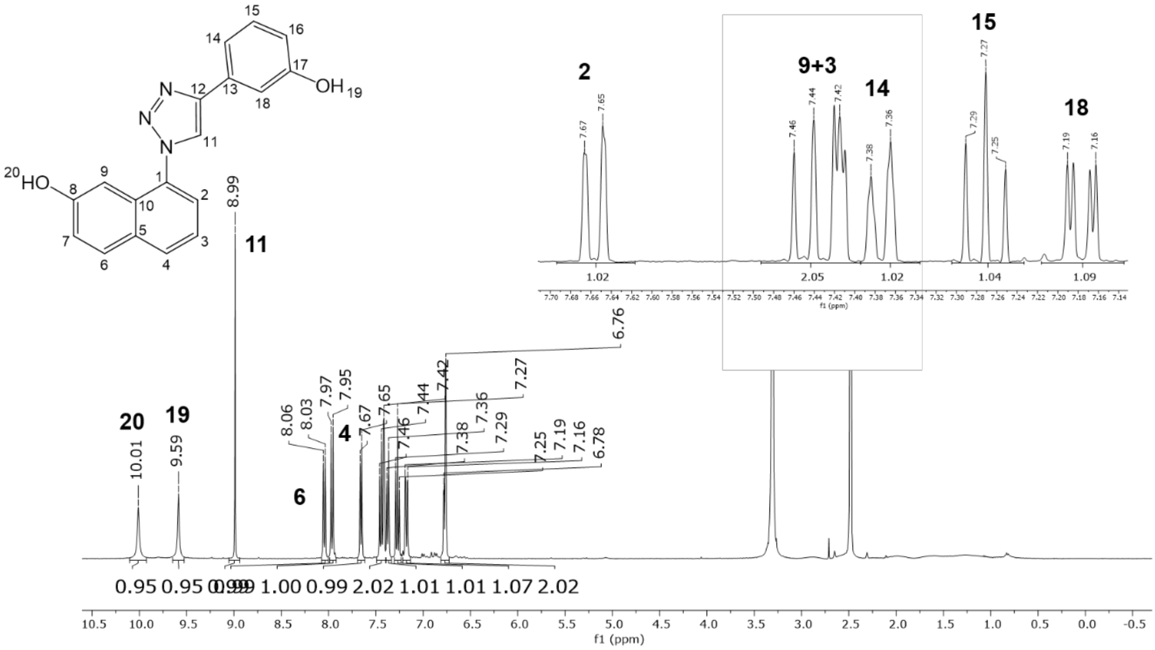


Figure S 35. ^{1}H-NMR spectra of compound (**4**) in DMSO-d$_6$.

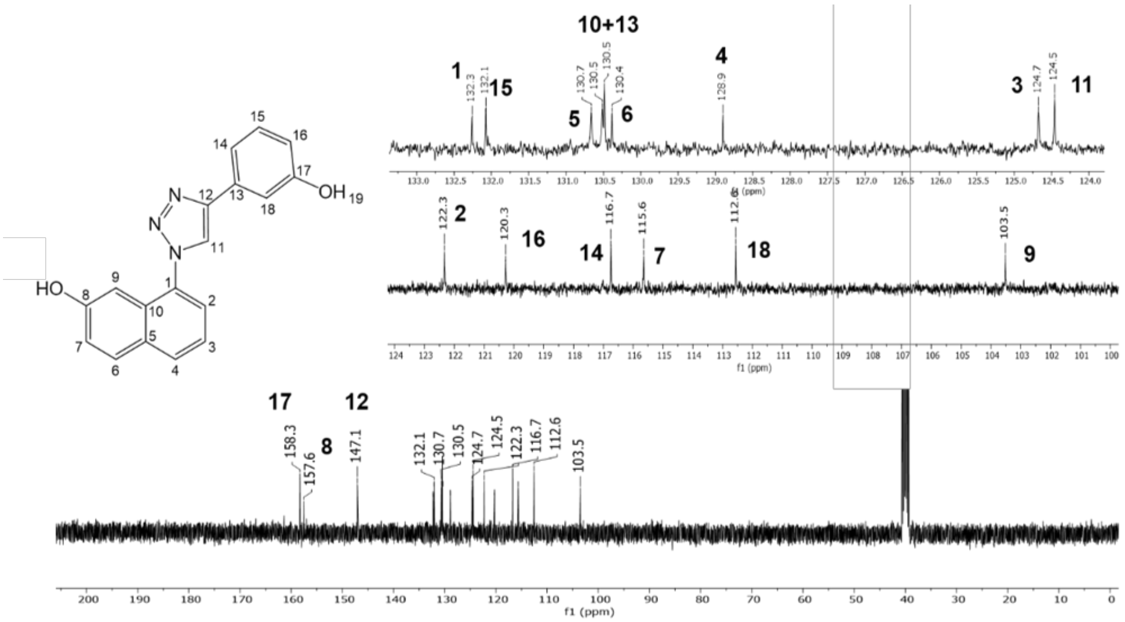


Figure S 36. ^{13}C-NMR spectra of compound (**4**) in DMSO-d$_6$.

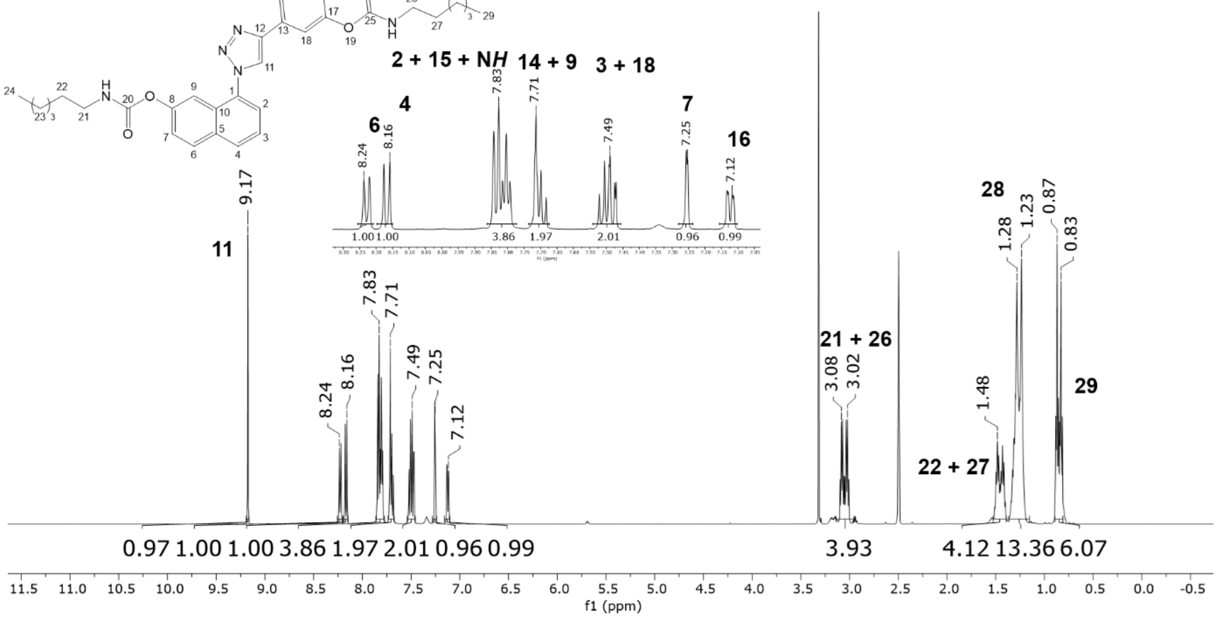


Figure S 37. ^{1}H-NMR spectra of compound (**4**) in DMSO-d$_6$.

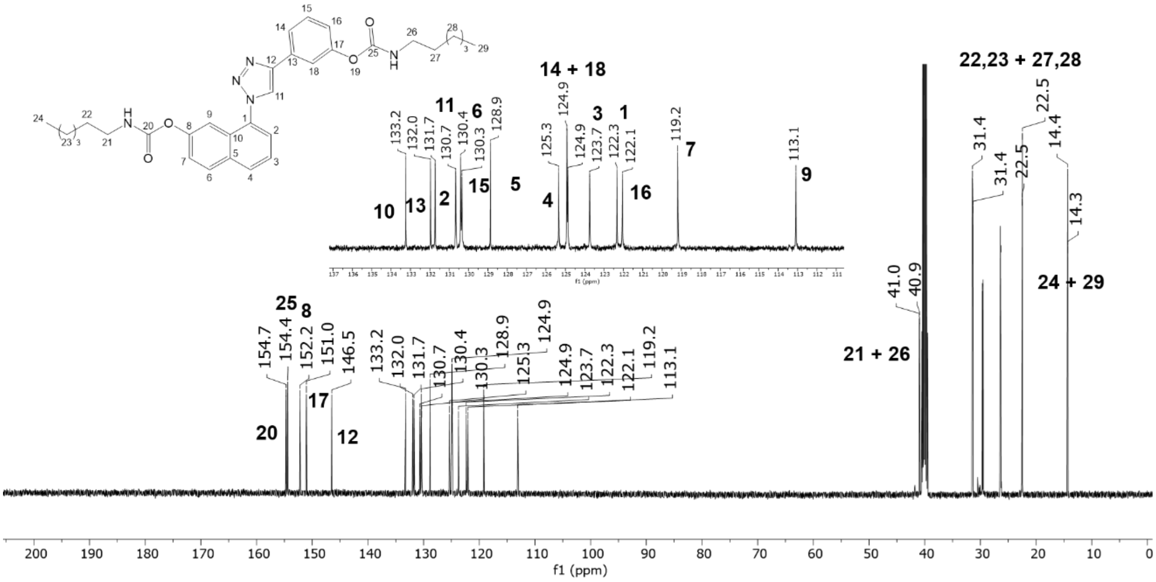


Figure S 38. ^{13}C-NMR spectra of compound (**5**) in DMSO-d$_6$.

8. ESI-TOF MS

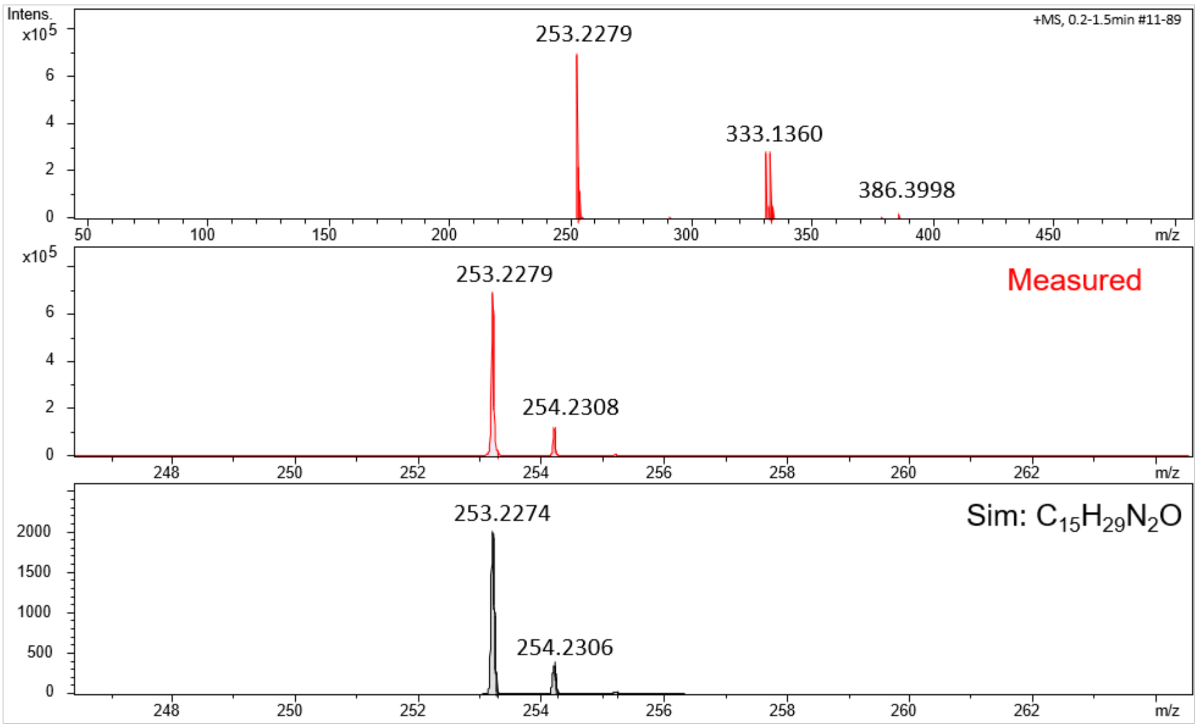


Figure S 39 ESI-TOF mass spectra 3-(11-hydroxyundecyl)-1-methylimidazolium bromide.

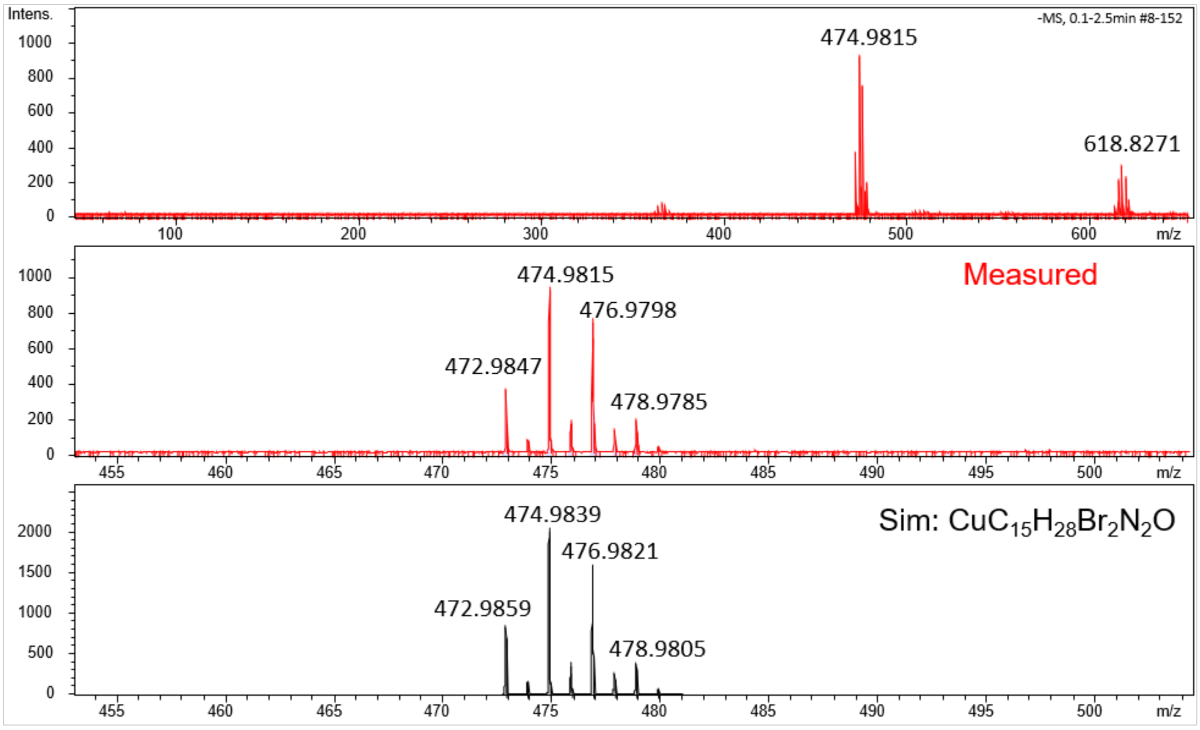


Figure S 40 ESI-TOF mass spectra of Cu(I) mono(NHC) complex.

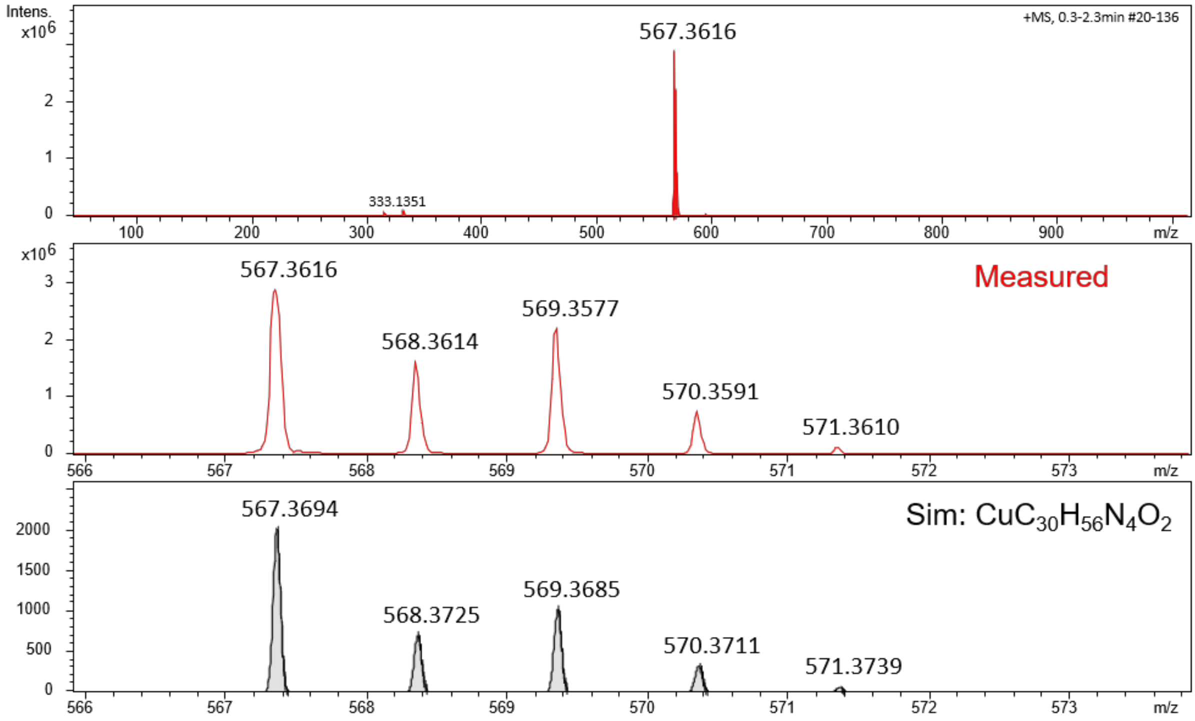


Figure S 41 ESI-TOF mass spectra of (**1**).

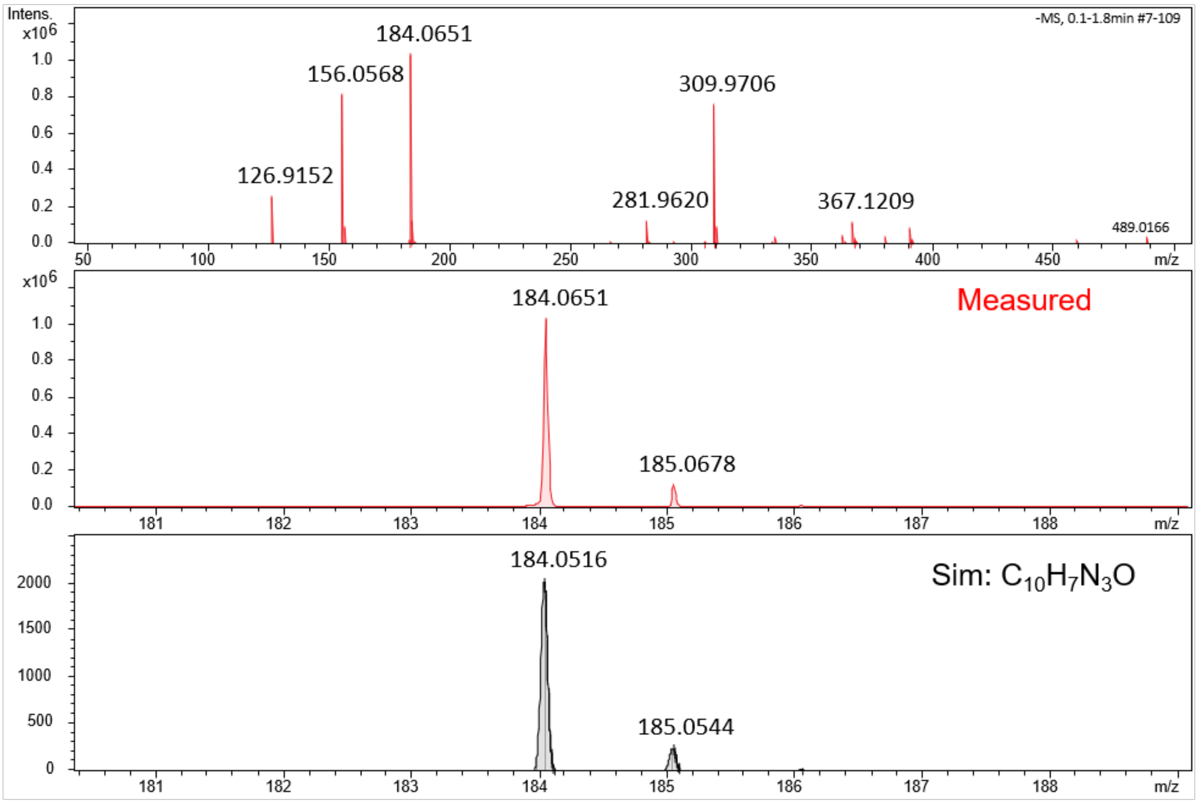


Figure S 42 ESI-TOF mass spectra of (**2**).

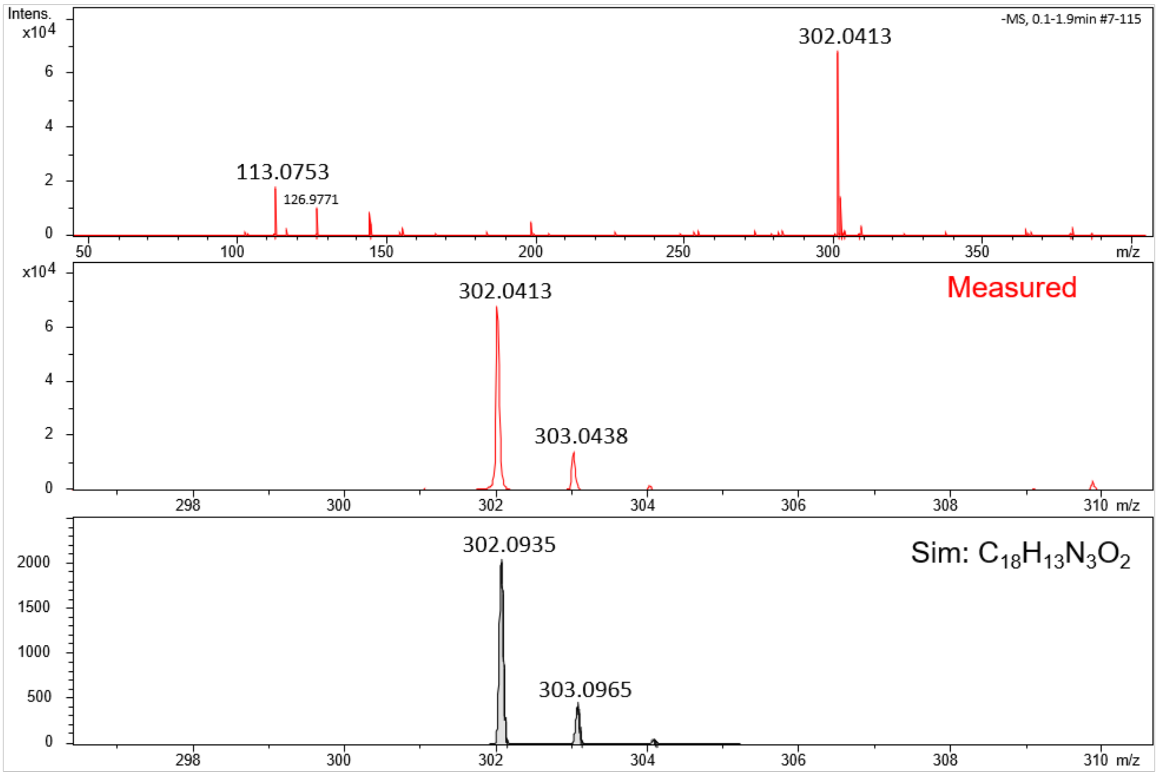


Figure S 43 ESI-TOF mass spectra of (**4**).

9. References

1. S. Yoshida, H. Suga and S. Seki, *Polymer Journal*, 1973, **5**, 25-32.
2. V. Kanyanta and A. Ivankovic, *Journal of the Mechanical Behavior of Biomedical Materials*, 2010, **3**, 51-62.